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The radiation hardness of Pr:LuAG scintillating ceramics

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Abstract

Scintillating ceramics have been considered to be used in upgraded HL-LHC (high luminosity large hadron collider) systems in high energy physics. However, the relationship between defects, annealing process, and radiation hardness still remains to be explored and understood. In this paper, Pr:LuAG ceramics were investigated as the promising scintillators due to the application requirements in HL-LHC, including the effects of ionizing irradiation, air annealing and sintering aids. Si^{4+} and Mg^{2+} were found to promote a concentration increase of oxygen vacancies without causing additional radiation induced color centers, while ionizing irradiation bring severe damage preventing light output. The Pr^{3+}/Pr^{4+} ions act not only as luminescent center, but also as compensator of intrinsic defects which could be attributed to the distinguish irradiation differences observed between Pr:LuAG and LuAG. Annealing was found to have an opposite effect on radiation induced absorption. From this study, it is confirmed that elimination of specific impurities from raw materials is a demanding step in ceramic optimization, and proper use of sintering aids could not only contribute to the ceramic transparency but also bring less harm to radiation hardness.

Keywords: Pr:LuAG ceramic; Radiation hardness; Sintering aids

1. Introduction

The discovery of new particles in high energy physics implies the development of calorimeter detectors based on scintillators. Besides quality criteria concerning luminescence efficiency, fast response, and energy resolution, good scintillators for high energy physics detectors are also expected to have good radiation hardness due to the high irradiation doses they are exposed [1]. Therefore, the R&D of radiation-hard materials working under harsh ionizing irradiation environments is a lively research field [2–4].

In application of medical imaging, Pr doped $Lu_3Al_5O_{12}$ (LuAG), which was first introduced in 2005, has attracted great attention for its good scintillator performance having high density (6.7 g/cm^3), fast decay time(~20 ns), high light yield (~20,000 ph/MeV) and excellent energy resolution of 4.6% [5]. Those demonstrated it a competitive scintillator. Moreover, transparent Pr:LuAG ceramics have been recently produced and investigated, showing even better application perspectives than single crystals [6,7]. However, aiming at applications of Pr:LuAG in high energy physics, its radiation hardness should also be evaluated and optimized. As for crystals, previous studies have shown that the desired radiation hardness can in principle be achieved by a careful control of the chemical stoichiometry and by the suppression of impurities at the ppm level [8]. For ceramic scintillators, no extended systematic studies were made concerning any kind of composition and the optimization of their radiation hardness is really a novel field of investigation.

A few studies appeared on radiation hardness processes of Pr:LuAG single crystal [3,4]. The radiation hardness of Nd:YAG ceramics was the subject of a recent investigation [9], and a report from CERN has revealed that Ce:(LuY)AG ceramics has demonstrated moderate radiation hardness for application in high energy physics [10]. However, no investigations have yet

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been reported for Pr doping. Therefore, the aim of this paper is to give the first insight on radiation damage processes in Pr doped LuAG ceramics, considering also the possible role of procedures usually adopted in ceramics preparation like the addition of sintering aids and the use of high temperature annealing after sintering.

2. Experimental

Pr:LuAG transparent ceramic samples were fabricated using the solid-state reaction method. Commercial powders of Lu_2O_3, Al_2O_3 and Pr_6O_{11} (>99.99% purity) were weighed according to the formula $Pr_{3x}:Lu_{3(1-x)}Al_5O_{12}$, $x=0.005$. From our previous study [7], such Pr concentration provided the highest scintillation efficiency. MgO and TEOS(Si) were used as sintering aids with contents of 0.01 wt% and 0.2 wt% respectively. Such sintering aids are known to be commonly used in transparent ceramic fabrication [11] in order to provide the best optical quality. After ball milling with ethanol for 10 h, the slurry was stove-dried, mesh-sieved and pressed to ceramic green bodies by isostatic cold pressing at 200 MPa. Fully densified ceramics were obtained after vacuum sintering at around 1800 °C for 10–20 h. An annealing process in air at 1450 °C for 10 h was then performed. The size of samples used for optical measurements was ∅=14 mm, 2 mm thickness. Prior to measurements they were polished up to optical grade.

Optical transmittance was measured by a Varian Cary 5000 spectrophotometer. Trace element analysis was conducted on ceramic samples using Inductively Coupled Plasma Optical Emission Spectrometer(ICP-OES,Vista AX, Varian). The energy spectra were collected by coupling the samples optically to a photomultiplier (Hamamatsu, R878) supplied by −1200 V bias. The shaping time was 750 ns. All samples were irradiated by 662 keV gamma rays using a ^{137}Cs source.

TSL measurements were obtained after X-ray irradiation with a Machlett OEG 50 X-ray tube operated at 30 kV. After irradiation, the samples were heated with a heating rate of 1 °C/s from room temperature (RT) up to 450 °C. The TSL emitted light was recorded with an EMI 9635 QB photomultiplier operated in photon counting mode.

For radiation induced optical absorption irradiations were performed by means of a ^{60}Co gamma source up to an absorbed dose of 2×10^5 Gy with a dose rate of about 1×10^4 Gy/h at room temperature, which was similar to that adopted also for the investigations on YAG crystal [12,13]. This irradiation dose is about 5 times higher than the one expected to be absorbed by ceramics in the HL-LHC calorimeter [10].

3. Results and discussion

By the X-ray diffraction method, it was proved that our Pr:LuAG ceramics are pure LuAG phase, and their good optical qualities revealed that the vacuum sintering had eliminated micropores to a very low content inside the ceramics [7]. Therefore in consideration of influencing factors on scintillation characteristics and radiation hardness, atomic scale defects would be expected to play key role, such as intrinsic color centers and impurity-related defects. Thus, the discussion carries out by considering the following three points which would occur during irradiation and give rise to radiation damage: (i) the population of electronic levels of point defects existing prior to irradiation, and of heterovalent impurity ions; (ii) the creation of new radiation-induced defects occurring especially by knock on collisions of heavy particles or by radiolysis; and (iii) the radiation-induced valence change of luminescent centers due to carrier capture.

First, after ceramic samples preparation the amount of impurities was measured by ICP-OES. In fact, Fe impurities are supposed to play a role in radiation damage of garnet crystals [12,14]. Moreover, Yb could also be found as it is known that it can be present as an unwanted impurity in Lu precursor raw material. Our results showed that the content of Yb ions is 16.6 ppm, while that of Fe ions is less than 3 ppm. On the other hand, the intentional doping with sintering aids, namely Si and Mg, should also be considered. A role of Si in the 2+ valence state in the formation of F^A centers was suggested to occur in YAG [15]. However, as far as its more probable 4+ valence state is considered, Si is not expected to give rise to oxygen vacancies [9]. At variance, Mg^{2+} incorporation implies charge compensation, which can be really fulfilled by oxygen vacancies. Such anionic vacancies can then act as electron traps during irradiation. As a matter of fact, in case of codoping with Mg and Si, the compensation can be in form of Si_{Al}, V'''_{Lu}, Mg'_{Al}, Vö. On the other hand, a self-compensation mechanism of both divalent and tetravalent impurities present in the crystal is not likely to happen due to the much higher formation energy confirmed by computer simulations [16]. Therefore it is likely to suppose that the concentration of oxygen vacancies is determined by Mg and heterovalent impurity ions (Fe^{2+} and Yb^{2+} in this case).

Fig. 1 reveals that pure LuAG ceramics with TEOS (Si) and MgO as sintering aids display different transmission characteristics after air annealing. An improvement of the transmittance above 300 nm is detected, accompanied however by a well evident absorption band in the 250 nm region. Such an absorption band could possibly be ascribed to Fe^{3+} [12,14].

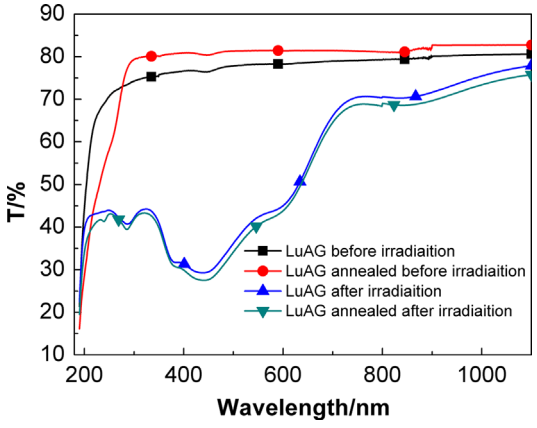

Fig. 1. Optical transmissions of both as prepared and annealed LuAG ceramics, before and after irradiation with ionizing radiation from a ^{60}Co gamma source.

Indeed, the ceramic sample was sintered under vacuum which could make Fe ions to be first stabilized as Fe^{2+}. After annealing in air, however, Fe^{2+} ions could be converted to Fe^{3+}. Moreover, due to the relative high amount of Yb impurities in the samples, Yb^{3+} can also be present in the sample after annealing. Therefore also the Yb^{3+} charge transfer transition occurring at 220 nm could contribute to absorption in the same region as Fe^{3+} [17]. So we attribute this absorption band to a combination of Fe^{3+} and Yb^{3+} ions transitions.

The transmittance of pure LuAG ceramics before and after irradiation was then measured. A pronounced transmission loss was observed: in order to reveal the absorption centers introduced by irradiation, values of radiation induced absorption coefficient (RIA) were calculated from the formula:

$$K = 1/d \ln(T_1/T_2) \quad (1)$$

where K is the absorption coefficient, d is the sample thickness and T_1 and T_2 are the transmissions of the sample obtained before and after gamma-irradiation, respectively.

As shown in Fig. 2, several radiation induced absorption centers are created while the annealing in air does not seem to influence strongly the spectra. Some bands, namely those at around 375 and 600 nm, have spectral positions similar to those detected in LuAG single crystals and which were ascribed to Yb^{2+} (4f–5d transitions) [3]. However, we observed a more severe damage in our ceramics with respect to single crystals, possibly due to the much higher irradiation dose used in our experiments. Moreover, we did not observe any specific additional absorption centers introduced by sintering aids, namely Si or Mg. As stated in the Introduction, sintering aids, especially Mg, could just promote the formation of certain intrinsic color centers like those of F-type.

We tentatively interpret the absorption in 220–250 region as a combination of Fe^{3+} charge-transfer transition and that of Yb^{3+}. Signatures of F^+ centers could be found at around 235 and 360 nm [18,19] while variants of F-type centers could also be responsible for the 430 and 880 nm absorption regions [15,20]. Moreover, contributions from O^- hole centers could also occur in the 300–600 nm region as suggested for YAG [18].

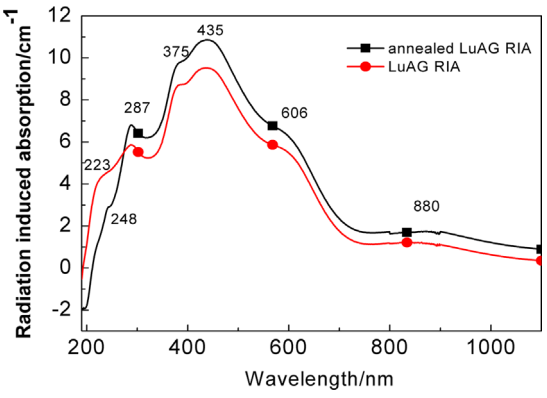

Fig. 2. Radiation induced optical absorption of LuAG ceramics before and after thermal treatment.

Finally, as mentioned above induced absorptions at around 375 nm and 600 nm are caused by 4f–5d transitions of Yb^{2+} ions [3].

As it is well known, the 5d–4f fast emission of Pr^{3+} covers the 300–400 nm range; therefore high transmission in this range is important to avoid self-absorption. In case of Pr:LuAG ceramics, unfortunately, we also observed great transmission loss after γ ray irradiation in Fig. 3. Here, we cut the data at 300 due to very strong noise caused by Pr^{3+} 4f–5d absorption. We also calculated the radiation induced absorption coefficient as shown in Fig. 4, and we found that the annealing process causes even higher absorption. Strong differences are however observed with respect to undoped specimens: the radiation induced absorption is positively lower, and the spectrum is dominated by the transitions at around 375 and 600 nm ascribed to Yb impurities, while signatures of intrinsic defects are no longer evidenced. This calls for a role of Pr ions in their reduction, whose microscopic mechanism is not clear. In as grown samples, Pr can effectively be incorporated in substitutional Lu position. Its tendency to become 4+ can contribute to reduce the concentration of oxygen vacancies. During irradiation, Pr can effectively trap holes so competing with hole capture by intrinsic hole defects.

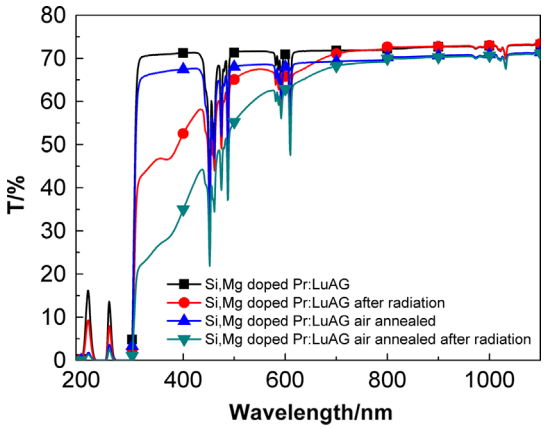

Fig. 3. Optical transmission of Pr:LuAG ceramics before and after irradiation with different thermal treatments.

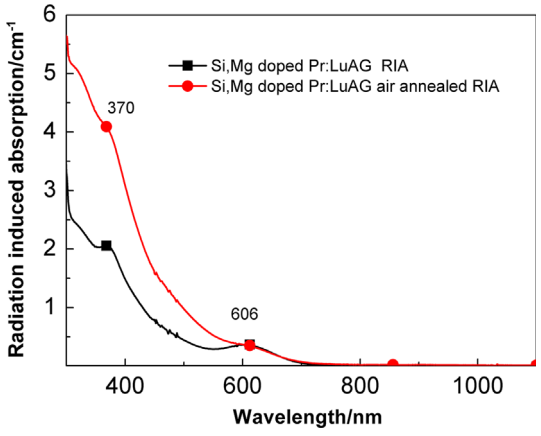

Fig. 4. Radiation induced absorption of Pr:LuAG ceramics with different thermal treatments.

The spectra have similar shape as those evidenced in Ce: LuAG [3]. However, the influence of radiation induced bands is expected to be stronger for Pr:LuAG, due to their higher superposition with the rare-earth ion emission spectrum which gives rise to a higher self-absorption.

To better understand defects in ceramics, we measured the TSL of different samples. In the region below RT, there are basically no differences between the two samples with and without annealing (not included in this paper). We only observed a broad peak quite similar to what we reported in [21]. In TSL measurements above RT, however, we noticed that all ceramics display a much higher signal than the single crystal. Such traps could also influence the radiation hardness of these two samples. Annealing strongly influences the trap configuration. In fact, the highest temperature peak at about 350 °C is strongly reduced after annealing pointing to the disappearance of the responsible defect. After irradiation, we further annealed the samples at 600 °C for 10 h.We observed full recovery of transmission of both LuAG and Pr:LuAG ceramics.

Since the TSL signal is reduced after annealing, while radiation induced absorption is increasing, we can suppose that traps and absorbing centers are distinct defects. However, they could be related during the recovery process occurring when heating at 600 °C after irradiation. For example, carriers initially stored in traps could be freed during heating and undergo recombination with carriers of opposite sign stored in optically absorbing centers, causing their return to the pre-irradiation configuration.Fig. 5.

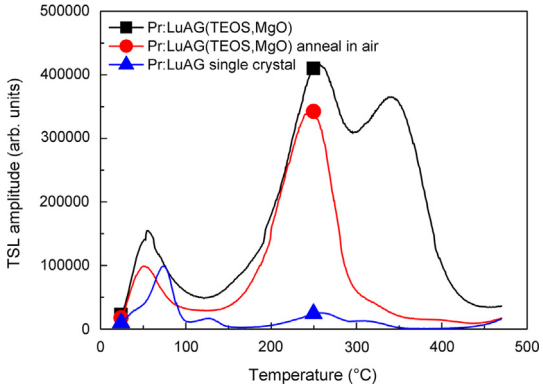

Fig. 5. TSL glow curves of single crystal and ceramic Pr:LuAG samples.

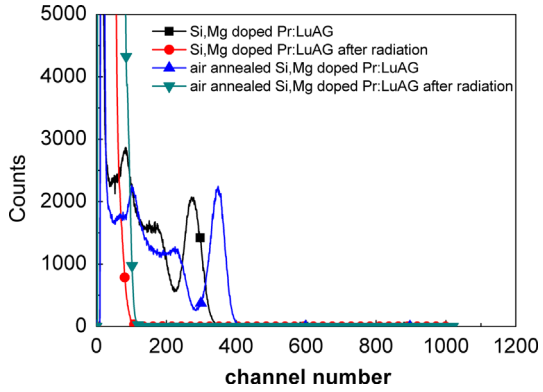

Fig. 6. Pulse-height spectra comparison of the 0.5 at% Pr:LuAG ceramic samples before and after irradiation with different thermal treatments.

Finally, we measured the light output of ceramic samples after different treatments. We found that the light output increased after annealing in air. However, after irradiation, both samples experienced severe damage. We did not detect any LY signal after irradiation. The high levels of ionizing irradiation cause great transmission loss in the emission region of Pr^{3+}, which in turn causes severe damage in light output. Fig. 6.

4. Conclusions

The effects of gamma-ray irradiation on optical transmittance of LuAG ceramics both undoped and doped with Pr have been discussed including the role played by annealing treatments. After exposure to a high dose of γ rays, both undoped LuAG and Pr:LuAG experienced severe damage. For undoped LuAG, it is manifested by a composite absorption spectrum featuring contributions from Yb and Fe impurities, and from intrinsic defect centers. After Pr-doping the contribution of intrinsic defects is markedly reduced and only impurity related bands dominate the radiation induced spectrum. Apparently sintering aids didn't introduce any additional absorption centers, while their role in increasing the concentration of intrinsic ones cannot be excluded. Annealing in air is responsible for an increase of radiation induced absorption. After irradiation, no light output signal was observed for Pr:LuAG irrespective of annealing treatments.

Parallel TSL studies revealed that ceramic samples display a much higher TSL signal than single crystal, and that the annealing process strongly decreases the concentration of the deepest traps. The different behavior of radiation induced absorption and TSL results suggest that absorbing centers have a different nature with respect to TSL-active defects, although they could be related in a thermally activated recovery process.

From the present results it can be concluded that the use of LuAG ceramics for high energy photons detection in harsh ionizing radiation environments should be considered only after further research work. Elimination of specific impurities from raw materials like Fe and especially Yb is a demanding step in material optimization. Our further study is going on the verification of the oxidation states of Fe and Pr by XPS or XAFS which is expected to be useful for deep understand of the nature of intrinsic defects and the influence of dopants, as well as their evolution under ionizing irradiations. Meanwhile, effect of thermal treatments in tuning their oxidation states and concentrations is also an interesting topic.

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References

[1] R.Y. Zhu, Precision crystal calorimetry in future high energy colliders, IEEE Transactions on Nuclear Science 44 (3) (1997) 468–476.

[2] R.H. Mao, L.Y. Zhang, R.Y. Zhu, Optical and scintillation properties of inorganic scintillators in high energy physics, IEEE Transactions on Nuclear Science 55 (4) (2008) 2425–2431.

[3] M.V. Derdzyan, K.L. Ovanesyan, A.G. Petrosyan, A. Belsky, C. Dujardin, C. Pedrini, E. Auffray, P. Lecoq, M. Lucchini, K. Pauwels, Radiation hardness of LuAG:Ce and LuAG:Pr scintillator crystals, Journal of Crystal Growth 361 (0) (2012) 212–216.

[4] T. Iwashita, K. Miyabayashi, Radiation hardness test of Pr:LuAG and BSO scintillators, IEEE Nuclear Science Symposium Conference Record (2010) 278–279.

[5] M. Nikl, H. Ogino, A. Krasnikov, A. Beitlerova, A. Yoshikawa, T. Fukuda, Photo- and radioluminescence of Pr-doped $Lu_3Al_5O_{12}$ single crystal, Physica Status Solidi A—Applied Research 202 (1) (2005) R4–R6.

[6] J. Pejchal, M. Nikl, E. Mihokova, J.A. Mares, A. Yoshikawa, H. Ogino, K.M. Schillemat, A. Krasnikov, A. Vedda, K. Nejezchleb, V. Mucka, Pr^{3+}-doped complex oxide single crystal scintillators, Journal of Physics D: Applied Physics 42 (5) (2009) 0055117.

[7] Y. Shi, M. Nikl, X.Q. Feng, J.A. Mares, Y.Q. Shen, A. Beitlerova, R. Kucerkova, Y.B. Pan, Q.A. Liu, Microstructure, optical, and scintillation characteristics of Pr^{3+} doped $Lu_3Al_5O_{12}$ optical ceramics, Journal of Applied Physics 109 (1) (2011) 013522.

[8] M. Nikl, A. Vedda, V. Laguta, Single crystal scintillation materials, in: G. Dhanaraj, K. Byrappa, V. Prasad, M. Dudley (Eds.), Springer Handbook of Crystal Growth, Springer, Berlin Heidelberg, 2010, pp. 1663–1700.

[9] A.J. Stevenson, B.C. Bittel, C.G. Leh, X. Li, E.C. Dickey, P.M. Lenahan, G.L. Messing, Color center formation in vacuum sintered $Nd_{3x}Y_{3-3x}Al_5O_{12}$ transparent ceramics, Applied Physics Letters 98 (5) (2011) 051906.

[10] D.L.G. Dissertori, F. Nessi-Tedaldi, F. Pauss, R. Wallny, Performance studies of scintillating ceramic samples exposed to ionizing radiation, in: the Proceedings of 2012 IEEE Nuclear Science Symposium Conference Record (Report number: ETHZ-IPP-2012-04), 2012, submitted for publication.

[11] Y. Li, S. Zhou, H. Lin, X. Hou, W. Li, H. Teng, T. Jia, Fabrication of Nd:YAG transparent ceramics with TEOS, MgO and compound additives as sintering aids, Journal of Alloys and Compounds 502 (1) (2010) 225–230.

[12] Y. Dong, G. Zhou, J. Xu, G. Zhao, F. Su, L. Su, H. Li, J. Si, X. Qian, X. Li, J. Shen, Color centers and charge state change in Ce:YAG crystals grown by temperature gradient techniques, Journal of Crystal Growth 286 (2) (2006) 476–480.

[13] Y. Zorenko, B. Pavlyk, R. Turchak, T. Zorenko, V. Gorbenko, I. Konstankevych, V. Savchyn, T. Voznyak, Influence of thermal treatment and radiation on absorption, luminescence and scintillation properties of single crystalline films, Radiation Measurements 42 (4–5) (2007) 557–560.

[14] C. Chen, G. Pogatshnik, Y. Chen, M. Kokta, Optical and electron paramagnetic resonance studies of Fe impurities in yttrium aluminum garnet crystals, Physical Review B 38 (13) (1988) 8555–8561.

[15] R. Gaume, Y. He, A. Markosyan, R.L. Byer, Effect of Si induced defects on 1 um absorption losses in laser-grade YAG ceramics, Journal of Applied Physics 111 (9) (2012) 093104.

[16] M.M. Kuklja, Defects in yttrium aluminium perovskite and garnet crystals: atomistic study, Journal of Physics: Condensed Matter 12 (13) (2000) 2953–2967.

[17] X. Zeng, X. Xu, X. Wang, Z. Zhao, G. Zhao, J. Xu, Effects of gamma irradiation and air annealing on Yb doped $Y_3Al_5O_{12}$ single crystal, Spectrochimica Acta A 69 (3) (2008) 860–864.

[18] M. Nikl, E. Mihokova, V. Laguta, J. Pejchal, S. Baccaro, A. Vedda, L. Juha, R.H. Sobierajski, H. Wabnitz (Eds.), in: Proceedings of SPIE European Symposium on Optics and Optoelectronics: Damage to VUV, EUV, and X-ray Optics, 2007.

[19] M. Springis, A. Pujats, J. Valbis, Polarization of luminescence of color centers in YAG crystals, Journal of Physics: Condensed Matter 3 (28) (1991) 5457–5461.

[20] A. Matkovskii, P. Potera, D. Sugak, L. Grigorjeva, D. Millers, V. Pankratov, A. Suchocki, Stable and transient color centers in $Gd_3Ga_5O_{12}$ crystals, Crystal Research and Technology 39 (9) (2004) 788–795.

[21] Y. Shen, Y. Shi, X. Feng, Y. Pan, J. Li, Y. Zeng, M. Nikl, A. Krasnikov, A. Vedda, F. Moretti, The harmful effects of sintering aids in Pr:LuAG optical ceramic scintillator, Journal of the American Ceramic Society 95 (7) (2012) 2130–2132.