The role of air annealing on the optical and scintillation properties of Mg co-doped Pr:LuAG transparent ceramics

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A B S T R A C T
Polycrystalline 0.2at%Pr:Lu3Al5O12 (Pr:LuAG) transparent ceramics were fabricated by solid-state reaction using 0.01 wt% MgO as sintering aid. The as-sintered ceramics were annealed in air at different temperatures. Optical absorption, photoluminescence, X-ray excited luminescence and pulse height spectra obtained after different annealing were compared. Modifications of the oxygen vacancy concentrations are found to govern the changes of the optical and scintillation response for annealing temperatures lower than 1000°C, while the oxidation of Pr^{3+} to Pr^{4+} plays a more important role for higher temperatures. Air annealing up to 700°C is an effective tool to improve the 5d-4f emission efficiency of MgO co-doped Pr:LuAG transparent ceramics. The highest radioluminescence intensity is obtained for the 700°C annealed sample. At variance, higher temperature annealing leads to the deterioration of 5d-4f photoluminescence and scintillation properties because of the self-absorption of Pr^{4+} and energy transfer from Pr^{3+} to Pr^{4+}. In addition, we find that the 4f-4f slow emission of ceramics shows different response characteristics under different irradiation sources.

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1. Introduction
The time-of-flight (TOF) technique was proposed with the goal to accurately detect high energy photons and particles in high energy physics [1], and to optimize image spatial resolution in medical imaging [2]. Scintillators with high light yield and fast decay are essential in the TOF technique for a satisfactory coincidence timing resolution to give precise TOF information [3]. For example, Lu2SiO5 (LSO) single crystal has a decay time of about 40 ns and has been commercially used in TOF-PET (positron emission tomography) [4]. Pr doped garnets, having a shorter decay time of about 20 ns, are also promising candidates for the TOF technique. Especially, Pr:Lu3Al5O12 was pointed out as a promising fast scintillator already in 2005 [5]. Apart from a fast scintillation decay time, Pr:LuAG has also other favorable properties. It features a high density of 6.7 g/cm³ which is important for X and γ-ray detection, as well as an outstanding energy resolution of 4.6% at 662 keV [6] that is beneficial for gamma ray discrimination [7]. It has been attracting much attention and is presently commercially used in Positron Emission Mammography (PEM) [8].

In the class of scintillators, other than single crystals, much research effort has been carried out on ceramics because of their superior properties such as homogeneous doping, lower price and easy production. (Y,Gd)₂O₃:Eu, Gd₂O₂S:Pr,Ce,F and (Lu,Tb)AG:Ce scintillation ceramics are being successfully used in computed tomography (CT) medical imaging [9–11]. Furthermore, many research works have been done in the field of new heavy and fast ceramic scintillators [12–14].

Solid state reaction is the most widely used method to prepare transparent ceramics due to its easy production and precise control of stoichiometry. Indeed, stoichiometry has an important influence on both the optical and scintillation properties [15,16] of LuAG...
transparent ceramics. An excess of Lu can work as “self-sintering aid” to obtain a satisfactory optical transmittance, but at the same time it is supposed to increase the concentration of $\text{Lu}_2\text{O}_3$ anti-site defects which, during irradiation with ionizing radiation, can trap free carriers from the conduction band and deteriorate scintillation properties. Sintering aids, especially $\text{SiO}_2$ and $\text{MgO}$, are usually employed to prepare garnet ceramics with good optical quality. Moreover, post-preparation annealing is usually conducted to remove oxygen vacancy related traps generated during the vacuum sintering process. Air annealing was proved to be an effective tool to improve the laser and scintillation properties of transparent ceramics [11,17]. A similar study was also performed on $\text{Pr:LuAG}$ single crystals [18] and it provided positive results. Besides the removal of oxygen vacancies, annealing in air may induce valence modifications of the rare earth luminescent dopant ions [19,20]. A recent investigation [21] proved that MgO sintering aid as well as post-preparation air annealing has a positive effect on the scintillation properties in Ce:LuAG ceramics. It was found that $\text{Ce}^{4+}$, induced by air annealing, is temporarily converted to $\text{Ce}^{3+}$ during irradiation giving rise to scintillation emission. In this process, $\text{Ce}^{4+}$ ions also compete with electron traps in carrier capture thus reducing their influence. Similar $\text{Pr:LuAG}$ with MgO as sintering aid, air annealing may lead to valence change of praseodymium to reach charge compensation just like Ce ions does in Ce:Mg:LuAG [20]. Therefore the influence of $\text{Pr}^{4+}$ on the luminescence and scintillation process in garnets is worth to be studied in detail. Given the position of the $\text{Ce}^{3+}$ and $\text{Pr}^{3+}$ ion ground states within the garnet forbidden gap [22] and related energy onset of charge transfer (CT) absorption processes at $\text{Ce}^{4+}$ and $\text{Pr}^{4+}$ centers [23–25], there is strong overlap between 5d-4f emission of $\text{Pr}^{3+}$ and CT absorption of $\text{Pr}^{4+}$ in single crystal LuAG host [26] which decreases scintillation light yield. Therefore $\text{Pr}^{4+}$ appears to be harmful to luminescence, and the balance between oxygen vacancy decrease and valence variation of Pr ion in the material during annealing is important. Thus, the effects of annealing as well as the valence control of Pr ion in Mg:Pr:LuAG are worth of deeper investigations.

In this work, Pr:LuAG transparent ceramics were fabricated using a small amount of MgO as a sintering aid, and subsequently annealed at different temperatures in air. Optical absorption, steady state and time resolved photoluminescence (PL) and X-ray excited luminescence (XEL) were performed to clarify the influence of oxygen vacancy and Pr$^{4+}$ modifications due to annealing.

## 2. Experimental

0.2at%$\text{Pr}_2\text{O}_3\text{Al}_2\text{O}_12$ transparent ceramics were fabricated by the solid-state reaction method with 0.01wt%MgO as sintering aid. Commercial powders of 4N purity $\text{Pr}_2\text{O}_3$, $\text{MgO}$, $\text{Lu}_2\text{O}_3$ and $\alpha$-$\text{Al}_2\text{O}_3$ powders were used as raw materials. The weighed powders were ball-milled for 12 h using alcohol as milling medium in corundum jar. The powder mixtures slurry was dried in oven at 70°C and then mesh-sieved through a 200-mesh screen. After removing the organic residues in the muffle furnace, the powder was dry-pressed into φ18 mm disks and then isostatically cold-pressed at 250 MPA. The green compacts were vacuum sintered at 1840°C for 30 h. Several as-sintered ceramic pieces were subsequently annealed at 700, 900, 1100, 1300 and 1500°C for 10 h in air, respectively. Finally, ceramics were mirror-polished on both surfaces into 1mm thickness for further tests.

The crystalline phase identification was performed by X-ray diffraction (XRD Rigaku Dmax-2200) using Cu Kα radiation ($\lambda = 0.15405$ nm) at 1.6 kW (40 kV, 40 mA). The micrographs of the powders and ceramics were observed with a field emission scanning electron microscopy (FESEM, SU8220, Hitachi, Japan). The optical transmittance and absorption spectra of mirror-polished samples was measured by a UV–VIS–NIR Spectrophotometer ( Cary 5000, Varian Inc, USA). In the text the data will be displayed in both transmittance and absorbance units. Photoluminescence (PL) measurements were investigated at room temperature using a Hitachi F-4600 Fluorescence Spectrophotometer equipped with a 150 W xenon lamp as the excitation source. Fluorescence decay curves were performed by a HORIBA Scientific Fluoro-Cube using time-correlated single-photon counting (TCSPC). The X-ray excited luminescence measurements were conducted by a home-made X-ray Excited Luminescence Spectrometer. The X-ray tube voltage was 70 kV. The emission spectra were corrected for the spectral sensitivity of the detection system using standard radon and tungsten lamps to remove the experimental distortions.

## 3. Results and discussion

Fig. 1 shows the SEM micrographs of the commercial starting powders and powder mixture after ball milling. $\text{Lu}_2\text{O}_3$ and $\text{Pr}_2\text{O}_3$ powders used are large aggregates composed of many nano-scale crystallites. The microstructure of $\text{Lu}_2\text{O}_3$ powder is relatively compact while the $\text{Pr}_2\text{O}_3$ powder is porous. $\alpha$-$\text{Al}_2\text{O}_3$ is relatively well disperses with primary particle size of about hundreds of nanometers. Fig. 1(d) shows that those large $\text{Lu}_2\text{O}_3$ and $\text{Pr}_2\text{O}_3$ particles can be well crushed and homogeneous mixture of the starting powders was achieved after 12 h milling.

Fig. 2 shows the XRD pattern of as-sintered Pr:LuAG ceramics. All the characteristic diffraction peaks of the sample could be satisfactorily indexed as the cubic garnet structure of LuAG (JCPDS73-1368), and there were no detectable secondary phase impurity peaks.

Fig. 3 shows the SEM micrographs of the thermally etched surface and of the fracture surface of as-sintered Pr:LuAG ceramics. The microstructure of the sample is homogeneous, no pores or secondary phases are observed at the grain boundaries or in the interior of the grains. The grain size of as-sintered Pr:LuAG ceramics obtained by the linear intercept method [27] was measured to be 14.6μm.

Fig. 4 shows the in-line transmittance and the photograph of the as-prepared and annealed Pr:LuAG ceramics. Text below the ceramics is clearly legible. The as-sintered Pr:LuAG ceramic sample shows a transmittance of 71.5% at 310 nm. For the samples annealed at 700°C and 900°C, the transmittances increase to 72.5% at 310 nm which may be due to slightly different surface qualities or sample inhomogeneities. When the ceramics were annealed at higher temperature, the transmittance gradually decreased in a wide spectral range below 800 nm, and induced yellowish-brown coloration in the 1300 and 1500°C annealed samples. It is ascribed to the charge transfer (CT) absorption from oxygen ligand to $\text{Pr}^{4+}$. The same coloration phenomenon was also seen in the MgO co-doped Pr:YAG [24] and Pr:LuAG [26] single crystals and other praseodymium containing compounds [28,29].

To further study the Pr:LuAG ceramics in detail, their absorption spectra are shown and discussed. Fig. 5(a) shows the absorption spectra of Pr:LuAG ceramic samples, as-sintered and annealed at different temperatures. The peaks located at 275nm and 240nm are due to the 4f-5d$\text{L}_2$ transitions of $\text{Pr}^{3+}$. Fig. 5(b) gives the difference spectra of samples annealed at different temperatures compared with the as-sintered ceramics. A slight absorption decrease below 300 nm is observed in the 700°C and 900°C annealed samples. We believe that it is partly caused by the removal of oxygen vacancy related deep defects which can cause additional absorption in this region [30,31]. However, the absorption amplitude starts to increase in a wide range after annealing at the temperatures above 700°C due to the increasing CT absorption of $\text{Pr}^{4+}$. Cut of 4f-5d$\text{L}_2$...