Optical Materials 66 (2017) 487–493

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Fabrication, microstructure and luminescence properties of Cr^{3+} doped $Lu_3Al_5O_{12}$ red scintillator ceramics

Yun Shi [a], Yu Zhao [a, b], Qiang Liu [b], Maoqing Cao [a, c], Peng Ma [a], Haohong Chen [a], Qian Liu [a], Jiang Li [a, *]

[a] Key Laboratory of Transparent and Opto-functional Advanced Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, 200050, China
[b] School of Materials Science and Engineering, Jiangsu University, Zhenjiang, 212013, China
[c] Institute of Crystal Growth, School of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai, 201418, China

ARTICLE INFO

Article history:
Received 8 January 2017
Received in revised form
23 February 2017
Accepted 27 February 2017

Keywords:
Red scintillator
Cr^{3+}:LuAG transparent ceramics
Vacuum sintering
Antisite defect

ABSTRACT

Cr^{3+} doped $Lu_3Al_5O_{12}$ transparent ceramics were developed as a new red scintillator ceramics. These ceramics were fabricated by a solid state reaction method under vacuum sintering at temperature range of 1550 °C–1890 °C for 10 h. The doping effect of different Cr^{3+} concentration (0, 0.1, 0.3 and 0.5 at. %) and air annealing effect were investigated as well. The transparent ceramics (70% @1 mm in visible light range) with dense microstructure were obtained when sintered at 1890 °C for 10 h, the average grain size of 0.3 at.% Cr:LuAG was calculated to be 7 μm. Photo-luminescence spectra revealed that there are two typical excitation bands at around 450 nm and 600 nm which were ascribed to the d–d transitions of Cr^{3+}. 0.3 at. % Cr:LuAG exhibited the optimum photoluminescence intensity and fast decay. Radio-luminescence under X-ray excitation indicated a characteristic Cr^{3+} emission peaking at 687 nm and 706 nm respectively. The Lu^{3+}_{Al} antisite defects related emission at around 300 nm was observed to decrease with the doping of Cr^{3+}. The steady luminescence efficiency (XEL spectrum integral) is around 20 times of the commercial BGO crystals, more important, the broad and continuous red emission between 600 nm and 800 nm demonstrated Cr:LuAG ceramics a prospective application as new red scintillators.

1. Introduction

Scintillators are able to detect high energy rays and particles (X-rays, γ-radiation, energetic particles or α, β particles etc.), when combined with photomultiplier tube (PMT) or photodiode (PD) in scintillator detectors [1,2], they could be used in medical nuclear imaging systems, i.e. X-CT (X-ray computer tomography) [3] or PET (positron emission tomography) [4] for diagnosis, in industry CT for non-destructive inspection, in high energy physics [5] for particle investigation and in well-logging [6] for energy exploration. The study on scintillators origins from 1900s [1]when the first scintillator $CaWO_4$ was introduced, hundreds of scintillators have been developed since then, representatively as NaI, $Bi_4Ge_3O_{12}$ (BGO), P_bWO_4 (PWO) and Ce:Lu_2SiO_5 (LSO) single crystals (SCs) [7]. By taking advance of the comparatively lower fabrication temperature with respect to that of single crystals, scintillator ceramics are considered to be strong competitors to single crystals in R&D of new scintillators, especially for materials having high melting temperatures. Since 1990s [7–9], Eu:$(Y, Gd)_2O_3$, Pr, Ce, F:Gd_2O_2S, Eu:Lu_2O_3 and Ce:$Y_3Al_5O_{12}$ (Ce:YAG) ceramics have been successively developed, some of them were put into practical use in commercial X-CTs. The dominant emission band of the above mentioned scintillators are mostly from 300 nm to 610 nm, the scintillators with emission near 400 nm are suitable for coupling with PMTs, while the others whose emissions are near 600 nm are suitable for photodiode/avalanche photodiode (PD/APDs) considering the different sensitive detection range of the photoelectric converter devices [7].

However, with the development of photoelectric converter devices [10,11], Si-Photodiode (SPD) [2] and Charge Coupled Device (CCD) [12,13] were also introduced in scintillator detectors, the sensitive detection range of which are between 600 nm and 800 nm. Besides, in recent years there are rising research interests in the red-to-NIR luminescence which is considered to be potential

* Corresponding author.
E-mail address: lijiang@mail.sic.ac.cn (J. Li).

http://dx.doi.org/10.1016/j.optmat.2017.02.061
0925-3467/

in vivo imaging [14] due to its higher transmittances of biological tissues (biological optical window), all the above drives the continuous searching of new scintillators having emissions beyond 600 nm.

$Lu_3Al_5O_{12}$ (LuAG) has a garnet cubic crystal system with space groups Oh10 (Ia3d), it is suitable for high transparent ceramics fabrication. Its high density (6.7 g/cm^3) and high effective atomic number (Z_{eff} = 63) means a higher stopping power than that of $Y_3Al_5O_{12}$ (YAG, 4.53 g/cm^3, Z_{eff} = 32.6) [15]. Rare earth ions Ce^{3+} and Pr^{3+} doped LuAG single crystal and ceramic have been extensively studied as fast scintillators due to the 5d-4f transition [8,15–18]. By codoping alkali ions Mg^{2+}, Liu et al. [19,20] demonstrated a superior scintillation performance in Ce:LuAG ceramics with respect to single crystal analogues. The 2D mapping of Pr:LuAG ceramics pixels is also available [21], but their dominant emission lies in around 550 nm (Ce:LuAG) and 310 nm (Pr:LuAG) respectively, which matches better with the traditional PMTs. Yanagida [2] summarized the study on Nd^{3+}, Eu^{2+}, Ho^{3+}, Er^{3+}, and Tm^{3+}doped LuAG due to their near infrared (NIR) emission from the 4f-4f transition. They were proposed to be suitable for systems (integrated-type detectors) reading out scintillation photons as a current with a few milliseconds of integration time, and in this case scintillators are not necessarily fast.

Besides rare earth ions, the transition metal ions Cr^{3+}/$Cr^{4+}$are also extensively studied as luminescence activators, works in LED [22] have proved the red emission of Cr^{3+} doped Ce:YAG, and in laser materials [23] infrared emission in Cr^{4+} doped Nd:YAG. The early introduction of Cr^{3+} as scintillator activators is Cr,Ce:$Gd_3Ga_5O_{12}$ ceramics in 1990s [8], in which case Cr^{3+} emitted 710 nm lighting by X-ray excitation and Ce^{3+} acted as a hole-trap to optimize the afterglow. Suzuki et al. [24] reported a study on Cr-doped $(Gd_XY_{1-X})_3Al_5O_{12}$ infra-red scintillator crystals (emission peak at 680 nm, 690 nm, 700 nm and 730 nm respectively). However, after the adding of Gd in YAG [24,25], dramatic reduction of the transparency occurred, it might be ascribed to the lattice distortion due to different ion radius. Yamaji et.al. [26] reported 0.5% Cr:$Y_3Ga_5O_{12}$ (YGG) crystals grown by the micro-pulling down method, they have a broad radio-luminescence emission peak at 716 nm, they could be applied as infrared scintillators, but the evaporation of Ga due to the high partial vapor pressure [27] is still a challenge to realize high transparency and strict stoichiometric ratio for Ga-containing garnet compounds. Comparatively, LuAG has proved its excellent performance as scintillator host [15] and high transparent LuAG ceramics were already technically available [17,18]. The present paper investigated the fabrication of Cr^{3+} doped LuAG transparent ceramics, the photo- and radio-luminescence were measured. The results point to the red scintillator-oriented applications.

2. Experimental procedure

2.1. Ceramics fabrication

High pure commercial powders, α-Al_2O_3 (99.95%, Alfa Aesar Corp.), Lu_2O_3 (99.99%, Harwk Corp.) and Cr_2O_3 (99.97%, Alfa Aesar Corp.), were weighted according to the chemical stoichiometry of $Lu_3(Cr_xAl_{1-x})_5O_{12}$, where x = 0, 0.001, 0.003 and 0.005, respectively. 0.03 wt % MgO (99.99%, Alfa Aesar Corp.) was added as a sintering aid. Those powders were mixed together by a high energy ball mill apparatus for 10–12 h at 200 rmp using alcohol as the ball milling medium. The slurry was dried in air at 70 °C for 1–2 h, and then sieved by a 200–mesh griddle. The obtained powders were calcined in 600 °C in a muffle furnace for 4 h to eliminate the possible introduced organic impurities. Circle ceramic green bodies with dimension of Φ20 mm × 2–5 mm were formed by 4 MPa uniaxial press and 200 MPa cold isotactic press, sequentially.

The ceramic green bodies were sintered in a pressureless vacuum furnace at temperature of 1550 °C–1890 °C for 10 h respectively, the heating process was started when the vacuum reached 10^{-3} Pa and it could further improve down to 10^{-4} Pa during the temperature holding process. The as–sintered ceramics were then annealed in air at 1450 °C for 10 h, and double-face polished up to an optical grade to thickness of 1 mm for further measurements.

2.2. Characterization

The phases of the obtained ceramics were detected by powder X-ray diffraction (PXRD) measurement after being ground into fine powders. The diffractometer is Huber G670 camera equipped with Cu target and Ge monochromater, which operates at 40 kV and 30 mA for CuKa1 radiation. The XRD measurements were executed at a step size of 0.005° in 2θ range of 10°–100°. The grain size and morphology of the ceramics were observed by a field emission scanning electron microscope (FESEM, SU8220, HITACHI). Before FESEM observation, the polished ceramics were thermally etched in air at 1500 °C for 3 h. In-line transmittance spectra were measured at a photometer (Cary5000, VARIAN), apparatus baseline was subtracted automatically. Photo-luminescence spectra and decay were measured by fluorescence spectrophotometer (FLS980, Edinburgh) under excitation of Xenon lamp. Radio-luminescence (RL) spectra were measured at a custom made fluorimeter excited by X-ray tube (70 kV, 1.5 mA). All the above measurements were conducted at room temperature.

3. Results & discussion

3.1. Microstructure and optical transmittance

Fig. 1 shows the photo of Cr:LuAG ceramics after vacuum sintering at 1890 °C for 10 h and air annealed at 1450 °C for 10 h, the Cr^{3+} doping concentrations are 0, 0.1, 0.3, 0.5 at.% (from left to right), respectively. It can be seen that the as-prepared Cr:LuAG ceramics (1.0 mm-thick) are transparent and deep green in color, while after air annealing the green color is getting slightly lighter, it might be due to the reduction of oxygen vacancies introduced during the vacuum sintering.

Fig. 2 is the XRD patterns of the Cr:LuAG ceramics with different Cr doping concentration (0, 0.1, 0.3, 0.5 at. %) after sintering at 1890 °C for 10 h, it can be seen that all the ceramics present a pure cubic garnet phase of LuAG (PDF No. 73–1368) without detectable second phase. From the XRD pattern, we calculated the lattice

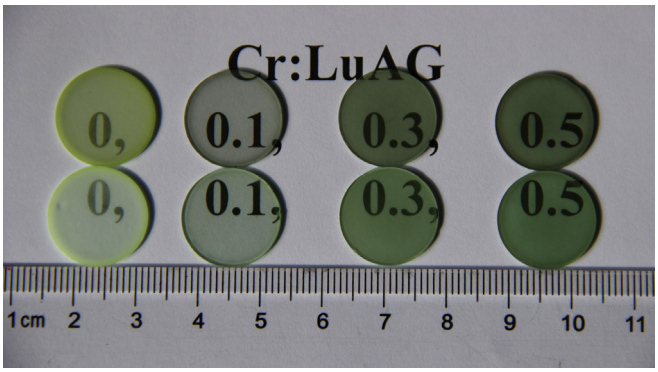

Fig. 1. Photograph of 0 at. %, 0.1 at. %, 0.3 at. % and 0.5 at. % Cr:LuAG transparent ceramics after vacuum sintering at 1890 °C for 10 h (the upper line) and the ceramics after air annealed at 1450 °C for 10 h (the lower line).