Fabrication of Ce\(^{3+}\) doped Gd\(_3\)Ga\(_3\)Al\(_2\)O\(_{12}\) ceramics by reactive sintering method

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1. Introduction

Scintillator materials were used to detect accelerative particles and high energy photons [1]. Compared with single crystal scintillators, polycrystalline ceramic scintillators have many advantages such as easy to realize the higher and uniform doping concentration of rare earth ions. Furthermore, large size of the ceramics can also be fabricated easily by using the advanced ceramic forming techniques. In recent years, three types of the ceramic scintillator materials including Eu: (Y,Gd)\(_2\)O\(_3\) (YGO, HitLight) [2], Ce: (Tb,Lu)\(_3\)Al\(_5\)O\(_{12}\) (Gemstone) [3] and Pr: Gd\(_2\)O\(_2\)S (GOS) [4,5], were mainly applied for commercial X-ray computed tomography (X-CT) systems. YGO and Gemstone ceramic scintillators were developed mainly applied for commercial X-ray computed tomography (X-CT) systems. YGO and Gemstone ceramic scintillators were developed for GE healthcare for their own X-CT systems, while GOS was widely used in X-CT systems by Hitachi [4], Toshiba [6], Philips [7] and Siemens [5].

In 2012, Ce: Gd\(_3\)Ga\(_3\)Al\(_2\)O\(_{12}\) (Ce:GGAG) single crystal was grown by K. Kamade et al. and their scintillator properties were also reported. Its light yield was about 46,000 ph/MeV and the energy resolution was 4.9% at 662 KeV [8]. As a novel type of scintillators, Ce:GGAG has many advantageous properties, such as high density (>6.0 g/cm\(^3\)), good chemical stability, fast luminescence decay, matching between the scintillator emission spectrum and photodetector, radiation resistance and etc. All of these properties made it an ideal scintillator for X-CTs. In additions, thanks to its cubic crystal structure, it can be sintered into transparent polycrystalline ceramics. Compared with growth temperature of the GGAG single crystals, the sintering temperature for GGAG ceramic is much lower. Therefore the volatilization of Gallium problem can be greatly suppressed in the fabrication process of the GGAG ceramics, which can contribute to the stoichiometric proportion control. Recently, Ce: GGAG ceramic scintillator was fabricated by N.J. Cherepy’s group, light yield of the ceramic is about 50,000 ph/MeV, and the energy resolution can reach 3\% – 5\% at 662 KeV [9,10]. In 2013, the ceramic of Ce: GAGG scintillator was fabricated by the Yanagida. Light yield of ceramic was reported to be 70,000 ph/MeV, which is much higher than that of corresponding single crystal (46,000 ph/MeV) [11]. In 2015, the Ce: Gd\(_3\)Al\(_3\)Ga\(_2\)O\(_{12}\) ceramics with good transparency were fabricated using ZrO\(_2\) as the sintering aids, which was reported by Jiang’s group [12]. In their studies, in order to reach the full density, the higher sintering temperature of 1650 °C was applied.

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ARTICLE INFO

Article history:
Received 30 June 2016
Received in revised form 3 August 2016
Accepted 3 August 2016
Available online xxx

Keywords:
Ceramics
Hot isostatic pressing
Reactive sintering
Ce\(^{3+}\): Gd\(_3\)Ga\(_3\)Al\(_2\)O\(_{12}\)

Abstract

Ce\(^{3+}\) doped Gd\(_3\)Ga\(_3\)Al\(_2\)O\(_{12}\) (Ce:GGAG) ceramics were fabricated by solid state reactive sintering method in this study. The ceramics were pre-sintered in normal muffle furnace in air at various temperature range from 1410 °C to 1550 °C for 10 h and post-treated by hot isostatic press at 1400 °C/2 h in 200 MPa Ar. The phase and microstructure evolution of Ce: GGAG samples during the densification process were investigated by X-ray diffraction and scanning electron microscope. Pure GGAG phase appeared with the temperature increased to 1200 °C. The fully dense and translucent GGAG ceramics were fabricated by pre-sintering at 1450 °C and followed by HIP treatment.

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In this paper, Ce: Gd3Ga3Al2O12 ceramic scintillator was fabricated by reactive sintering method in a simple muffle furnace in air. The ceramics can be fully densified by pre-sintering at 1450 °C, followed by the hot isostatic pressing (HIP) treatment at 1400 °C/2 h in 200 MPa Ar. The phase structure and the microstructure evolution of Ce:GGAG was also investigated.

2. Experiment

2.1. Fabrication of the powder and ceramics

High-purity Gd2O3 (99.99%, Jiahua Advanced Materials Resources Co., Ltd, China), Ga2O3 (99.999%, FDC, China), Al2O3 (99.99%, Taiimei Chemicals Co., Ltd, Japan), CeO2 (99.995%, Alfa Aesar, UK) powders were used as the starting materials. They were weighted in accordance with the composition of (CexGd1-x)(GayAl1-y)5O12. No any sintering aid was used. The x was fixed at 0.0025, and the y was fixed at 0.6. After weighting, these powders were mixed in Nylon milling jar by planetary ball-milling method with high purity Al2O3 balls for 15 h in ethanol. The rotation speed was kept at 180 rpm. The powder mixtures were obtained by drying in oven at 55 °C/24 h and sieved through 100 mesh screen. The green bodies were shaped with stainless steel die using the dried powder at 20 MPa, and were further treated by cold isostatic pressing (CIP) at 200 MPa for 5 min. The green bodies were sintered at different temperatures from 1410 °C to 1550 °C in Muffle furnace in air. Finally, the ceramics were treated by HIP at 1400 °C.

2.2. Characterization

The sample densities were tested by the Archimedes method using the electronic balance (BSA6235-CW, Sartorius, Germany). Phase compositions and its evolution of the samples were identified by X-ray diffraction (XRD, D2, Bruker, Germany) using CuKα radiation. The microstructures of the samples were performed by scanning electron microscope (SEM, JSM-6510, JEOL, Japan).

3. Result and discussion

3.1. The characterization of the powder

The morphology of the powders before and after ball milling was illustrated in Fig. 1. It can be found from Fig. 1 (A) that heavily aggregated large Ga2O3 rod and Ga2O3 fine particles co-existed in the original powders. Strong agglomerated Gd2O3 and CeO2 particles were observed in Fig. 1 (B) and (C). The average size of the original Ga2O3 powders was about 5 μm and CeO2 powder show the large particle size of around 10–20 μm. The Al2O3 powder shows the very fine particle size of less than 200 nm in Fig. 1 (D). It can be observed from Fig. 1 (E) that the pretty uniform powder mixtures with the particle size less than 1 μm were achieved after ball milling.

3.2. The phase formation, densification and microstructure evolution of Ce:GGAG ceramics

The XRD patterns of the Ce:GGAG samples pre-sintered at various temperatures were shown in Fig. 2. It can be found that the pure GGAG phase cannot be one-step formed by the directly reaction of the Ga2O3, Ga2O3, and Al2O3. During the sintering process, various intermedium phases such as Gd3GaO5, Gd4Al2O9, GdAlO3, and GdAlO3 formed subsequently. When the sintering temperature

![Fig. 1. The SEM images of Ga2O3 (A), Gd2O3 (B), CeO2 (C), Al2O3 (D) and the powder mixtures after ball milling (E).](image)

![Fig. 2. XRD patterns of the ceramics sintered at different temperatures.](image)