Journal of the European Ceramic Society xxx (2016) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

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

Characterization in activators' distribution and photoluminescence properties of Ce^{3+} doped MgAlON transparent fluorescent ceramic

Xin Liu, Bowen Chen, Bingtian Tu, Hao Wang*, Weimin Wang, Zhengyi Fu

State Key Lab of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

ARTICLE INFO

Article history:
Received 18 December 2015
Received in revised form 24 March 2016
Accepted 1 April 2016
Available online xxx

Keywords:
Ce^{3+} doped
MgAlON
Transparent ceramic
Photoluminescence
Grain boundaries

ABSTRACT

A novel Ce^{3+} doped MgAlON transparent ceramic with high transparency in UV-VIS-NIR regions was fabricated by pressureless sintering. The highly dense transparent ceramic was colorless in sight. Under the excitation of the UV light, the fluorescent ceramic emitted a blue light with spectrum centered at 420 nm, which was caused by the 5d-4f energy transition of Ce^{3+}. The fluorescent ceramic exhibited slight thermal quenching at 200 °C with 77% of the intensity at room temperature. The result of fluorescent lifetime measurement indicated there existed two emission centers in the sample. By combining with the cathodoluminescence (CL) mapping method, the Ce^{3+} ions were demonstrated to be in two regions: a. most of them existed in the expanding regions of grain boundaries; b. the residual ones were located in the lattices of the host grains.

1. Introduction

Due to the combination of excellent optical and mechanical properties of transparent ceramics, such as AlON [1], MgAlON [2], spinel [3] and YAG [4], the investigations on fabrication and application of them have drawn much attentions for decades. Generally, the transparent ceramics with high transmittance in whole visible region possess wide-enough band gaps [5]. Thus, most of the above transparent ceramics are potential to be applied as host materials for activator ions which usually consist of relatively narrower energy level structures [6]. By doping of these activators, functionalized transparent ceramics with diverse and bran-new properties in novel application fields could be obtained [7–10].

With the increasing demand of high-power white light emitting diodes (LED), the YAG:Ce based glass ceramics and transparent ceramics have been developed in past years [8,11]. Therein, these functionalized ceramics possessed not only the additional optical property originated from doping of functional ions but also the various advantages of the host transparent ceramics, including high transparency, good mechanical property and thermal conductivity, which could overcome the shortages of commercially used phosphor-in-silicon LED devices [8]. Under the excitation of blue light, the YAG:Ce emits a yellow light, which is caused by the 5d-4f energy transition of Ce^{3+} located in Y-O dodecahedral sites. Moreover, the light emission behaviors of Ce^{3+} ions is seriously affected by their local environments, i.e. the coordination numbers and ions. In other words, by adjusting the transparent ceramic host, it is reliable to prepare the functionalized transparent ceramic exhibiting new luminescence properties.

The spinel-type oxynitrides, like AlON, MgAlON, were frequently studied as phosphors by doping of activator ions [12–16]. While most of the studies focused on the powder state, especially for the commonly used Ce^{3+} ions, seldom work was aimed at its doping behaviors in these spinel-type oxynitride transparent ceramics. In our previous works, highly transparent MgAlON transparent ceramics with good mechanical properties had been fabricated, which were demonstrated to be an ideal host for activitors [2,9]. To clarify the photoluminescence (PL) properties and the distribution behavior of Ce^{3+} in the MgAlON transparent ceramic, in this work, the highly transparent Ce^{3+} doped spinel-type oxynitride MgAlON ceramic, whose chemical formula is $Mg_{0.27}Al_{2.58}O_{3.73}N_{0.27}$, had been firstly fabricated by pressureless sintering. The phase composition, microstructure, element distribution and optical properties of the specimen were investigated respectively. Moreover, the temperature-dependent emission property, energy absorption and transition mechanisms of the ceramic were analyzed.

2. Experimental procedures

In this work, uniform and fine $Mg_{0.27}Al_{2.58}O_{3.73}N_{0.27}$ (MgAlON) ceramic powders were previously-prepared by solid-state reac-

---

* Corresponding author.
E-mail address: shswangh@whut.edu.cn (H. Wang).

http://dx.doi.org/10.1016/j.jeurceramsoc.2016.04.001
0955-2219/© 2016 Elsevier Ltd. All rights reserved.

Please cite this article in press as: X. Liu, et al., Characterization in activators' distribution and photoluminescence properties of Ce^{3+} doped MgAlON transparent fluorescent ceramic, *J Eur Ceram Soc* (2016), http://dx.doi.org/10.1016/j.jeurceramsoc.2016.04.001

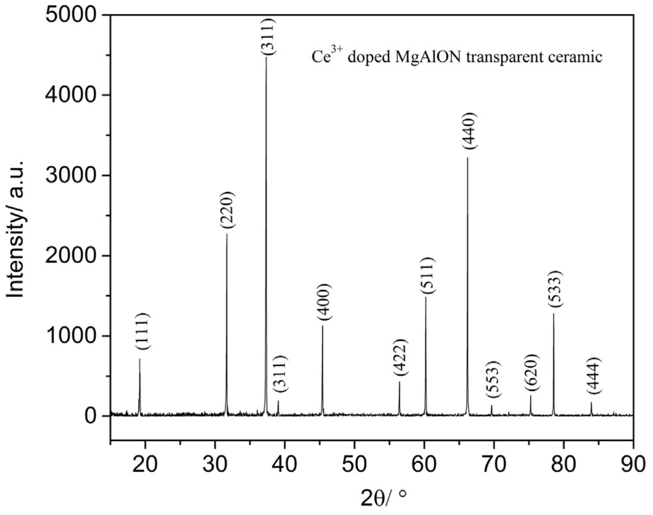

Fig. 1. XRD pattern of synthesized Ce^{3+} doped MgAlON transparent ceramic.

tion process [2]. The prepared MgAlON powders were mixed with 0.02 wt% CeO_2 (>99.99%) by ball-milling with quadruple weight of highly pure Al_2O_3 balls and anhydrous alcohol media for 12 h. Then, the mixtures were dried and sieved. The as-prepared powders were firstly dry-pressed into a disk of 20 mm in diameter and 4 mm in thickness by a uniaxially pressure of 20 MPa, and then cold isostatically pressing treated at 180 MPa. Subsequently, the obtained green body was sintered at 1875 °C for 24 h in N_2 atmosphere, and then freely cooled inside the graphite furnace to room temperature. Finally, the sintered sample was ground to 2 mm in thickness and mirror-polished.

The phase composition of as-prepared ceramic was obtained by the X-ray diffractometry (XRD; X'pert PRO of Panalytical, Almelo, Netherlands) with a stepping rate of 2/min. The scanning electron microscope (SEM; S-3400, Hitachi, Tokyo, Japan) was employed to characterize the microstructure of sample's etched surface. The UV–vis spectrophotometer (UV-2550, Shimadzu, Kyoto, Japan) and Fourier transmission infrared absorption spectroscopy (FT-IR; Thermo Nicolet 6700, Thermo Nicolet Corporation, Washington, USA) were used to measure the transmittance of sample in both UV–vis and near-infrared region respectively. The photoluminescence spectrum at room temperature (RT), decay time and temperature-dependent emission spectra from RT to 250 °C were recorded by a fluorophotometer (FLS920, Edinburgh Instruments, Livingston, UK). The CL mapping image and spectrum of the unetched ceramic surface were recorded by a field-emission gun scanning electron microscope (FESEM, Quanta 200F, FEI, Oregon, USA) combining with a CL device (Mono Cl3+, Gatan, California, USA).

3. Results and discussion

The graphite furnace could provide a reducing atmosphere at high temperature in N_2, which would assist to reduce the Ce^{4+} into the trivalent one. The XRD pattern (Fig. 1) of the Ce^{3+} doped MgAlON transparent ceramic is well corresponded to the un-doped MgAlON ceramic [2], and there is no apparent secondary phase detected in the doped ceramic under the XRD detection limitation.

Fig. 2a shows the microstructure of the surface of chemical-etched ceramic, revealing the grains are large with sizes ranged from 10 to 50 μm, which is in agreement with reports of transparent ceramics with long-time sintering periods. The grain boundaries are clear and clean that no apparent secondary phase could be seen. The specimen is very dense that few residual pores could be observed from the SEM image. The measured density is 3.637 g/cm^3 by Archimedes method, which is close to the calculated theoretical density of 3.646 g/cm^3 of the un-doped MgAlON within the experimental error. The CL mapping of luminescence centers with a monitor wavelength of 422 nm (by inserted CL spectrum) is illustrated in Fig. 2b. Most of the emitting sites are uniformly distributed in grain boundaries (white line in Fig. 2b), while scarcely any parts are located in grains. In other words, almost all the Ce^{3+} disperse along the grain boundaries of doped ceramic, which is familiar in other rare-earth doped ceramics [9,17,18]. In fact, compared to the radius of Al^{3+} (51 pm), the rare-earth ions are generally much larger in size, e.g. Eu^{2+} (109 pm) and Ce^{3+} (103 pm), which could be hardly implanted into the lattice of the ceramic. Instead, the grain boundaries with confusion arrangement of atoms could accommodate more [19].

The UV excitation and emission spectra of doped ceramic are shown in Fig. 3a. The excitation spectrum consists of two major peaks locating at 260 and 340 nm respectively. The absorption band centered at 260 nm is due to the rare-earth doping generated host defect absorption followed by a rapid energy migration to Ce^{3+}, while the band from 270 to 400 nm is attributed to the trivalent cerium's 4f-5d charge transfer transition. The emission curve consists of a broad band ranging from 360 to 570 nm with one characteristic peak centered at 422 nm, which is similar with that shown in CL spectrum, and supposed to be aroused by the energy transition from vast different crystal field-splitting components of the excited 5d energy level to the ground-state of Ce^{3+}. Compared with the emission spectrum in $MgAl_2O_4$: Ce [10], a red shift in MgAlON: Ce makes the emission spectrum primarily located in the blue light region. That is because, for the two similar spinel-structure ceramic hosts, the partial substitution of nitrogen for oxygen coordinated to rare-earth ions would change the crystal field [20] resulting in a more severely splitting of the 5d level of Ce^{3+}, and may generate some lower level in field-splitting components that lead to the red shift. As shown in the inserted picture of Fig. 3a, the excited ceramic emits bright blue light under the excitation of a 330 nm UV lamp in a dark room. Consequently, the MgAlON: Ce transparent ceramic is reckoned as a promising blue light emission phosphor, which is capable of being excited by commonly used UV chips.

To further investigate the luminous mechanism of the doped ceramic, the decay time at 330 nm UV excitation is recorded. Fig. 3b shows the decay time and the exponential fitting curve. The solid line is well fitted to two exponentials according to the Eq. (1):

$$I(t) = I_0 + \alpha \times e^{-t/\tau_1} + \beta \times e^{-t/\tau_2} \quad (1)$$

where τ is the decay time. The fitted τ (τ_1, τ_2) are 4.31, 31.99 ns and take up 26%, 74% of the recombination center respectively. The obvious difference in decay time indicates that the Ce^{3+} ions are located in two distinct local environments. Therein, the faster decay time (τ_1) at 4.31 ns is close to that of the α-stimulated $MgAl_2O_4$: Ce scintillator at 4.55 ns. Thus, the Ce^{3+} ions corresponding to the τ_1 should stay in the similar sites in $MgAl_2O_4$: Ce [10]. In the view of the small solubility limit of rare-earth ions in spinel-type transparent ceramic grains [21], the τ_1 corresponded emitting sites ought to be located in lattices. The slower τ_2 takes most parts in the emitting centers. By combining with the CL mapping result, it should be attributed to the Ce^{3+} distributed along the grain boundary. Emitting center in these expanding regions could generate some kinds of delayed excitation caused by thermally released electrons or holes trapped by lattice defects. Therefore, the afterglow is the main origin of τ_2.

The thermal quenching is one of the most important parameters for phosphors. Fig. 4 shows the temperature-dependent luminescent properties at the temperature ranging from 37 to 250 °C. The decrease of emission intensity is apparent under heating condition. As the increase of temperature, the nonradiative transition caused

Please cite this article in press as: X. Liu, et al., Characterization in activators' distribution and photoluminescence properties of Ce^{3+} doped MgAlON transparent fluorescent ceramic, *J Eur Ceram Soc* (2016), http://dx.doi.org/10.1016/j.jeurceramsoc.2016.04.001