Journal of Solid State Chemistry 184 (2011) 1405–1414

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

Structure and photoluminescence properties of Ce^{3+}-doped novel silicon-oxynitride $Ba_{4-z}M_zSi_8O_{20-3x}N_{2x}$ (M=Mg, Ca, Sr)

Y. Fang [a], Y.Q. Li [a,b,*], R.J. Xie [b], N. Hirosaki [b], T. Takade [b], X.Y. Li [a], T. Qiu [a]

[a] College of Materials Science and Engineering, Nanjing University of Technology, New Model Road 5, Nanjing, Jiangsu 210009, China
[b] Nitride Particle Group, Nano Ceramics Center, National Institute for Materials Science, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

ARTICLE INFO

Article history:
Received 1 January 2011
Received in revised form
21 March 2011
Accepted 26 March 2011
Available online 13 April 2011

Keywords:
Alkaline earth silicon-oxynitride
Cerium
Crystal structure
Luminescence properties
Thermal quenching

ABSTRACT

Structural and photoluminescence properties of undoped and Ce^{3+}-doped novel silicon-oxynitride phosphors of $Ba_{4-z}M_zSi_8O_{20-3x}N_{2x}$ (M=Mg, Sr, Ca) are reported. Single-phase solid solutions of $Ba_{4-z}M_zSi_8O_{20-3x}N_{2x}$ oxynitride were synthesized by partial substitutions of $3O^{2-}\rightarrow 2N^{3-}$ and Ba→M (M=Mg, Ca, Sr) in orthorhombic $Ba_2Si_4O_{10}$. The influences of the type of alkaline earth ions of M, the Ce^{3+} concentration on the photoluminescence properties and thermal quenching behaviors of $Ba_3MSi_8O_{20-3x}N_{2x}$ (M=Mg, Ca, Sr, x=0.5) were investigated. Under excitation at about 330 nm, $Ba_3MSi_8O_{20-3x}N_{2x}$:Ce^{3+} (x=0.5) exhibits efficient blue emission centered at 400–450 nm in the range of 350–650 nm owing to the $5d\rightarrow 4f$ transition of Ce^{3+}. The emission band of Ce^{3+} shifts to long wavelength by increasing the ionic size of M due to the modification of the crystal field, as well as the Ce^{3+} concentrations due to the Stokes shift and energy transfer or reabsorption of Ce^{3+} ions. Among the silicon-oxynitride phosphors of $Ba_3MSi_8O_{18.5}N$:Ce^{3+}, $M=Sr_{0.6}Ca_{0.4}$ possesses the best thermal stability probably related to its high onset of the absorption edge of Ce^{3+}.

1. Introduction

Since metal–silicon-oxynitride compounds have been found to be novel hosts of luminescent materials, rare earth activated silicon-oxynitride phosphors have been extensively studied in recent years due to their high potential applications for LED lighting and display [1–4]. In metal silicon-oxynitrides, alkaline earth silicon-oxynitride phosphors have been drawn much more attention because of their high efficiency and high chemical and thermal stability for use as wavelength conversion phosphors for near-UV and blue-LED devices [5–8]. Under UV and blue light excitation, Eu^{2+}-doped alkaline earth silicon-oxynitride materials can emit blue to yellow light, depending on the type of alkaline earth ions and the crystal structure. For example, $MSi_2O_2N_2$:Eu^{2+} emits greenish-yellow light (~560 nm) for M=Ca, green light (~540 nm) for M=Sr, and blue-green light (~500 nm) for M=Ba [6]. As an oxygen-rich oxynitride phosphor, $Ba_3Si_6O_{12}N_2$:Eu^{2+} shows green emission at about 525 nm with a peak width (FWHM) of about 68 nm [9]. Whereas as a nitrogen-rich oxynitride phosphor $BaSi_6N_8O$:Eu^{2+} is a blue-green emitting phosphor with emission peak at about 500 nm [10] due to a different crystal structure. In contrast, Ce^{3+}-doped alkaline earth silicon-oxynitride only shows blue emission and the absorption of Ce^{3+} is normally limited in UV region; for example, under excitation in UV range (300–360 nm), $MSi_2O_2N_2$:Ce^{3+} emits UV-blue and blue light with a broad emission band peaking at about 392, 396, and 473 nm for M=Ca, Ba, and Sr, respectively [11]. Similar to oxide based phosphors, in comparison with Eu^{2+} the $5d\leftrightarrow 4f$ transition of Ce^{3+} is always located at higher energy in alkaline earth silicon oxynitride phosphors in the same hosts.

Recently, a few investigations have been reported about the preparation of oxynitride phosphors through the approaches of the cross-substitution of $(AlO)^+\rightarrow(SiN)^+$, as well as the unequivalent substitution of $3O^{2-}\rightarrow 2N^{3-}$, starting from the oxide based hosts, such as alkaline earth aluminosilicate and alkaline earth silicate compounds [12–15]. From a structural viewpoint, a large number of alkaline earth silicates are highly promising to be incorporated by nitrogen into the silicate host lattices to form new silicon-oxynitride materials, which enables us to use them as novel hosts of luminescent materials.

In the present work, we selected an oxide-based orthorhombic $Ba_2Si_4O_{10}$ [16] or $BaSi_2O_5$ [17] as a mother compound and then partially replaced oxygen by nitrogen using Si_3N_4 as nitrogen source. To our best knowledge, apart from several studies on the luminescence properties of $BaSi_2O_5$:Eu^{2+} [18] (with similar crystal structure of $Ba_2Si_4O_{10}$ [16,17]), the

---

[*] Corresponding author at: College of Materials Science and Engineering, Nanjing University of Technology, New Model Road 5, Nanjing, Jiangsu 210009, China

E-mail address: y.q.li@njut.edu.cn (Y.Q. Li).

0022-4596/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2011.03.048

photoluminescence properties of Ce^{3+}-doped silicon-oxynitride based on the orthorhombic structure of $Ba_2Si_4O_{10}$ by partial replacement of O with N have not yet been reported so far. Therefore, in this work we investigate on the synthesis of Ce^{3+}-doped $Ba_{4-z}M_zSi_8O_{20-3x}N_{2x}$ $(0 \le x \le 1)$ (M=Mg, Ca, Sr) by a solid state reaction at high temperature using alkaline earth carbonates, silicon nitride, silicon oxide and cerium oxide as raw materials. The phase formation and the crystal structure were analyzed by X-ray powder diffraction. The microstructure of the phosphors was observed by scanning electron microscopy. Subsequently, the photoluminescence properties and the thermal stability of Ce^{3+}-doped oxynitride phosphors have been discussed in detail.

2. Experimental procedures

2.1. Synthesis

Undoped and Ce^{3+}-doped alkaline earth silicon-oxynitride phosphors of $Ba_{4-z}M_zSi_8O_{20-3x}N_{2x}$ were prepared by a solid state reaction with the starting material of Si_3N_4 (SN-E10, Ube Industries, Ltd., Tokyo, Japan), SiO_2 (Kojundo, Chemical Laboratory Co. Ltd., Japan), $BaCO_3$ (Sigma-Aldrich, 99.5%), MgO (Konoshima Chemical Co. Ltd., Osaka, Japan), $CaCO_3$ (Kojundo, Chemical Laboratory Co. Ltd., Japan), $SrCO_3$ (Sigma-Aldrich, 99.95%), and CeO_2 (Shin-Etsu Chemical Co. Ltd., Japan, purity $>99.99\%$). The concentration of the activator ion of Ce^{3+} in $Ba_{4-z}M_zSi_8O_{20-3x}N_{2x}$ is set as related to the total molar amounts of Ba and M. The appropriate amounts of raw materials were weighed out according to the stoichiometric formulations and then homogeneously mixed in a silicon-nitride mortar and pestle. The powder mixtures were pressed into a pellet and fired in a BN boat at 1050–1300 °C in a horizontal tube furnace under a firing atmosphere of N_2–H_2 (5%). The firing temperature depends on the composition and the activator concentration of Ce^{3+}. After firing, the samples were cold down to room temperature in the furnace and then ground into powder for the subsequent characterizations.

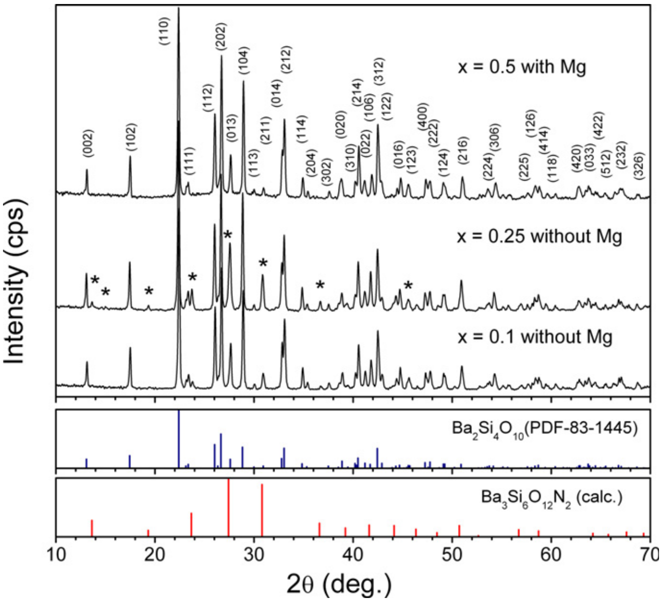

Fig. 1. X-ray powder diffraction patterns of $Ba_{4-z}Mg_zSi_8O_{20-3x}N_{2x}$ (from bottom to top z=0, 0, and 1). The asterisks indicate the impurity phase of $Ba_3Si_6O_{12}N_2$.

2.2. Characterizations

The phase formation of the synthesized materials was analyzed by X-ray powder diffraction (XRD) carried out at the condition of 40 kV and 40 mA with Cu$K\alpha$ radiation (RINT 2000, Ultima III, Rigaku, Japan) in the 2θ range of 10–70° by normal scanning with the speed of 2°/min. As regard to the Rietveld refinements, the data were collected by a step scanning mode with a step size of 0.02° and a count time of 6 s per step in the range of 10–100°. The Rietveld refinements were carried out by the GSAS package [19,20]. The structural parameters of a single crystal $Ba_2Si_4O_{10}$ [16] were adopted as an initial model for the refinement of the crystal structure of $Ba_{4-z}M_zSi_8O_{20-3x}N_{2x}$ (x=0.5, z=1). The Ce and N ions are supposed to be randomly occupied on Ba and O sites in $Ba_2Si_4O_{10}$, respectively, in the course of the Rietveld refinements.

The morphology and particle size of the silicon-oxynitride phosphor were observed by scanning electron microscopy (JEOL, JSM-5900, Japan).

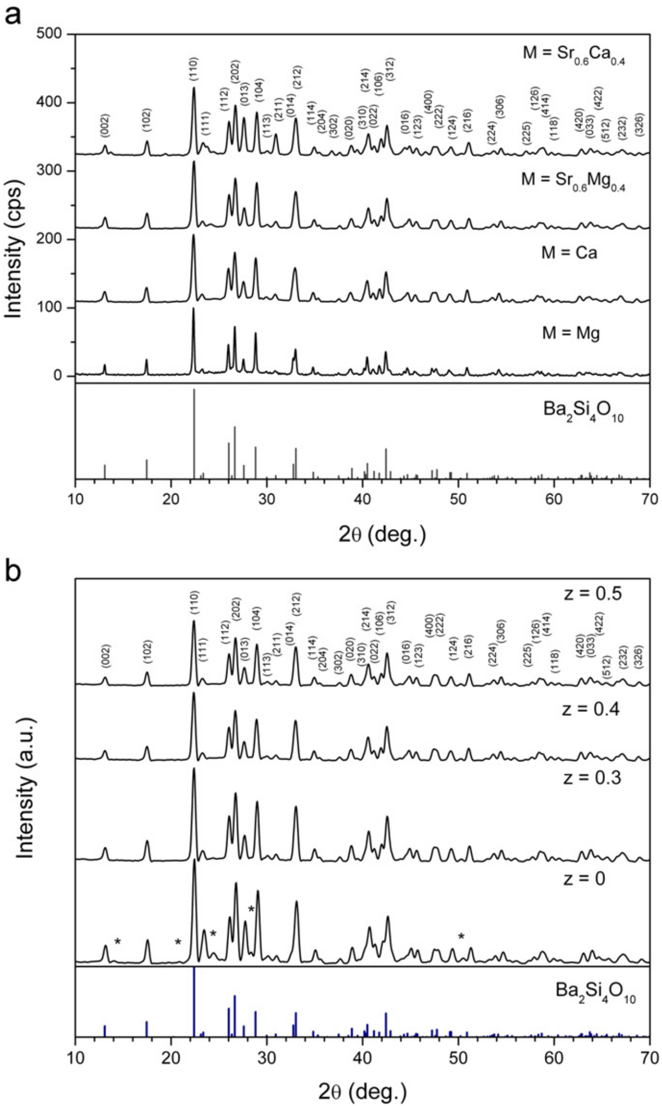

Fig. 2. (a) X-ray powder diffraction patterns of $Ba_{2.94}MCe_{0.04}Si_8O_{18.5}N$ (Ce=1 mol%, M=Mg, Ca, $Sr_{0.6}Mg_{0.4}$, $Sr_{0.6}Ca_{0.4}$). (b) X-ray powder diffractions of $Ba_{2.94}Sr_{1-z}Mg_zCe_{0.04}Si_8O_{18.5}N$ at different z (the asterisks are the impurity phase of $Ba_3Si_6O_{12}N_2$).