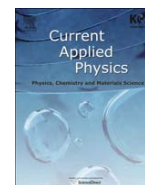




Contents lists available at ScienceDirect

Current Applied Physics

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Preparation and photoluminescence properties of Ce doped lutetium silicate nanopowders by sol–gel method

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ARTICLE INFO

Article history:

Received 3 September 2010

Accepted 2 November 2010

Available online 12 November 2010

Keywords:

Lutetium silicate

Cerium

Sol–gel

Photoluminescence

Lu_2SiO_5

ABSTRACT

Cerium doped lutetium silicate powders were prepared by sol–gel process with different cerium concentrations (0, 0.01 and 0.03 mol%). The synthesized lutetium silicate powders were investigated by X-ray diffraction (XRD), TG-DTA, SEM, and Photoluminescence excitation and emissions. The crystallization of lutetium silicate is observed at 1.073 °C in S2 (and S3: 1.058 °C) sample. The formation of lutetium silicate phases was confirmed by XRD analysis for the powders heated at 1.200 °C, of which mixed phases containing Lu_2SiO_5 and $\text{Lu}_2\text{Si}_2\text{O}_7$ phase were observed. Lutetium silicate powders were homogeneous and constituted of small spherical particles of about 400 nm. Lutetium silicate powder itself was not scintillate, but scintillation yield was higher in $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ powder. Very broad spectra were observed in the range of 350–530 nm, and emission intensity increases at a Ce doping of 0.01%, but decreases at 0.03%.

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1. Introduction

Lutetium oxyorthosilicate doped cerium materials were initially studied as a powder for cathode ray tube phosphor [1]. C.L. Melcher et al. discovered that $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ was a new kind of promising scintillation crystal. It exhibits a superb light yield (273,300 photons/MeV) and high density (7.4 g/cm³) and a fast scintillations decay time (~40 ns) as well as suitable emission wavelength (420 nm) [2,3]. So it can be used for gamma ray detection in nuclear medical diagnostic instruments, and high energy and nuclear physical experiments. It is now replacing BGO ($\text{Bi}_4\text{Ge}_3\text{O}_{12}$), conventional scintillator, in positron emission tomography (PET). Therefore, the investigation on the growth and scintillation properties of $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ materials has become an attractive and interesting field in the past decade. Most studies and applications of $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ materials are hindered by difficulty that crystal is grown into large size at high temperature. Lutetium oxyorthosilicate crystals were grown by Czochralski method [4,5], of which the cost is very high, and the maximum reachable concentration of Ce ion is quite low.

Lutetium oxyorthosilicate doped cerium powder and films have also been reported to be made by sol–gel processing recently [6,7]. A sol–gel process has been developed to produce LuBO_3 doped with various rare earth ions [8]. Bescher et al. proposed a sol–gel route to lutetium-containing scintillator, but the scintillating phase was embedded in an amorphous matrix and was not clearly identified [9]. A sol–gel processing is a promising candidate to make $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ powders and films, and offer several unique advantages. The molecular precursors are used to control the morphology and texture the powders and thin films. Moreover, the sol–gel route is used to elaborate materials of different composition in various concentrations, and the sol–gel derived materials are synthesized at lower temperature than the ones elaborated by classical solid-state synthesis. In general, the synthesis of $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ materials using Czochralski method and the scintillation characteristics has been well studied [4,5,10]. However, $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ materials have been synthesized rarely using sol–gel method, and the scintillator characteristics are not fully understood. Therefore, when it clarifies the synthesis of $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ materials using sol–gel method and scintillator characteristics, it is important to investigate crystal structures with dopant concentrations. An original sol–gel route has been developed in our laboratory for elaboration of CdWO_4 and scintillation properties of sol–gel derived CdWO_4 materials have been reported recently [11,12]. In this paper, the characteristic of sol–gel derived Lu_2SiO_5 powders doped with Ce^{3+} is reported.

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Table 1
Nominal composition of $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ scintillator (unit: mol%).

Sample	Compound	$\text{Lu}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$	$\text{Si}(\text{OC}_2\text{H}_5)_4$	$\text{Ce}(\text{NO}_3)_2$	$i\text{-C}_3\text{H}_7\text{OH}$
S1	Lu_2SiO_5	1	1	0	20 ml
S2	$\text{Lu}_2\text{SiO}_5:0.01\text{Ce}^{3+}$	1	1	0.01	20 ml
S3	$\text{Lu}_2\text{SiO}_5:0.03\text{Ce}^{3+}$	1	1	0.03	20 ml

2. Experimental

$\text{Lu}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ (Wako Pure Chemical Industries Ltd., Japan), $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS, Jassen Chemical, Japan), $\text{Ce}(\text{NO}_3)_2$ (Junsei Chemical Co. Ltd., Japan) and $i\text{-C}_3\text{H}_7\text{OH}$ (Showa Chemical Co. Ltd., Japan) were used as the starting materials. The nominal composition of each sample was summarized in Table 1. $\text{Si}(\text{OC}_2\text{H}_5)_4$ was at first hydrolyzed by dissolving it into the 10 ml of $i\text{-C}_3\text{H}_7\text{OH}$ solution under vigorously stirring at 40 °C for 1 h. $\text{Lu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_2$ were dissolved separately in 10 ml of $i\text{-C}_3\text{H}_7\text{OH}$, and then two solutions were mixed together, as shown in Table 1. The mixed solution was vigorously stirred at 25 °C for 2 h, and a clear precursor sol was obtained by completely mixing the reactants. The transparent solution was allowed to form a gel at 65 ± 5 °C and the gel was dried at 110 ± 5 °C for 24 h. A gel was formed after a few days, of which color was turned into light yellow and transparent. This gel was then fired at 1.200 °C for 2 h in order to obtain $\text{Lu}_{2(1-x)}\text{Ce}_x\text{SiO}_5$ (x : 0, 0.01 and 0.03) crystalline powder. During heating, the temperature was held at 300 °C for 2 h to remove the residual organic compounds.

The thermal behavior of the dried gel was investigated using TG-DTA (STA 409, Netzsch, Germany), and carried out at up to 1.200 °C in air at a constant heating rate of 5°/min using Al_2O_3 as a reference material. XRD (Philips PW1077, U.S.A., $\text{CuK}\alpha$, 30 kV, 20 mA) analysis was conducted to identify the crystalline phase of $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ powders. The morphologies and element distribution of $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ powders were observed in both SEM (Hitachi, S-4300, Japan) and EDS (Horiba EMAX 2770, Japan). Emission spectra were measured using fluorescence spectrophotometer (Perkin–Elmer, LS-55B, U.S.A.). The excitation source and wavelength was Xe lamp and wavelength 356 nm.

3. Results and discussion

Fig. 1 shows the thermal analysis of the precursor gel for S2 sample. The evolution of $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ from the amorphous to

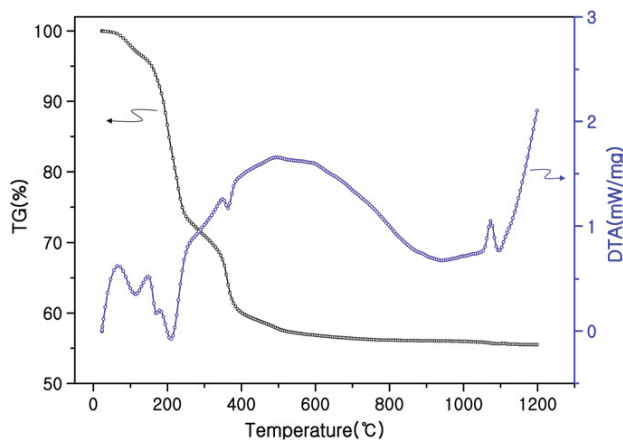


Fig. 1. Thermal analysis of $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ powders (S2) synthesized by sol–gel process.

crystalline form has been studied by thermal analysis. This study gives informations on the crystallization of the lutetium silicate. The first derivative is also shown in order to clearly identify the temperatures associated with the different weight losses. The first weight loss is observed at around 150 °C and can be allotted to the elimination of adsorbed species, such as alcohol or water molecules. Some residual organic compounds can also be directly pyrolyzed. The second significant weight loss, observed at about 350 °C, attributes to the decomposition of nitrates and organic radicals. The last weight loss and a sharp exothermic peak are observed at 1.073 °C in S2 (and S3: 1.058 °C) sample and correspond to the crystallization of Lu_2SiO_5 phase [9]. Total weight loss is approximately 44%. It is important to note that this crystallization temperature is well below temperatures required by the Czochralski method (about 2.000 °C) and also well below temperatures and times required for the solid-state synthesis of Lu_2SiO_5 from Lu_2O_3 and SiO_2 powders (about 1.400 °C) [3,13].

Fig. 2 shows the X-ray diffraction patterns for Lu_2SiO_5 powders (S3) heated at 500, 800, 1.000 and 1.200 °C, respectively. The gel powder remained amorphous up to 500 °C. It was seen that Lu_2O_3 phase appeared at 800 °C, increasing crystallinity as the heating temperature was increased. At 1.000 °C, Lu_2SiO_5 phase begins to be mainly formed. The formation of Lu_2SiO_5 phases was confirmed by XRD analysis for the powder heated at 1.200 °C, of which mixed phases containing Lu_2SiO_5 and $\text{Lu}_2\text{Si}_2\text{O}_7$ phase were observed. It has also been observed that when doping Lu_2SiO_5 with Ce^{3+} up to the doping of 0.03 mol%, but Lu_2SiO_5 phase is formed more in 0.01 mol% than in the doping of 0.03 mol%.

Fig. 3 shows the morphology of Lu_2SiO_5 powders heated 1.200 °C for 2 h and shows the agglomerates of approximately 400 nm of particles having a relatively narrow size distribution. Fig. 3 (c) and (d) shows the morphology and EDS of Lu_2SiO_5 powders (S3 sample) heated at 1.200 °C for 2 h. Lu_2SiO_5 powders are homogeneous and constituted of small spherical particles of about 400 nm. The size distribution of particles is very uniform. Fig. 3(d) shows that the surface of gel powders was doped efficiently with Ce^{3+} .

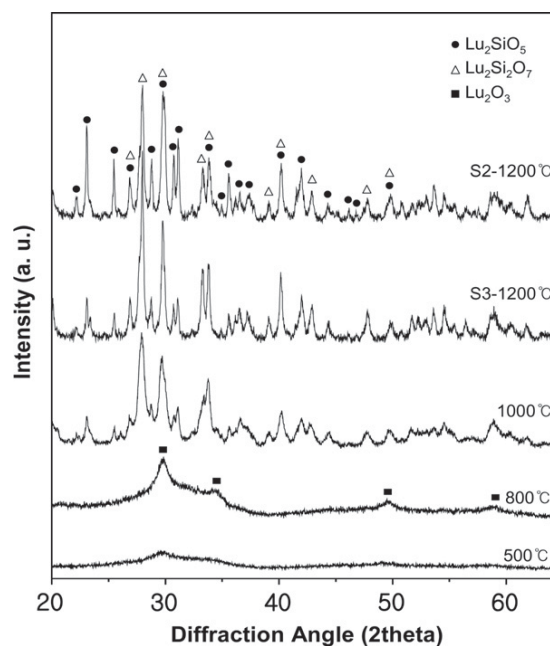


Fig. 2. X-ray diffraction patterns of $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ powders (S3) heated at different temperatures and $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ powders (S2) heated at 1.200 °C (the upper part).

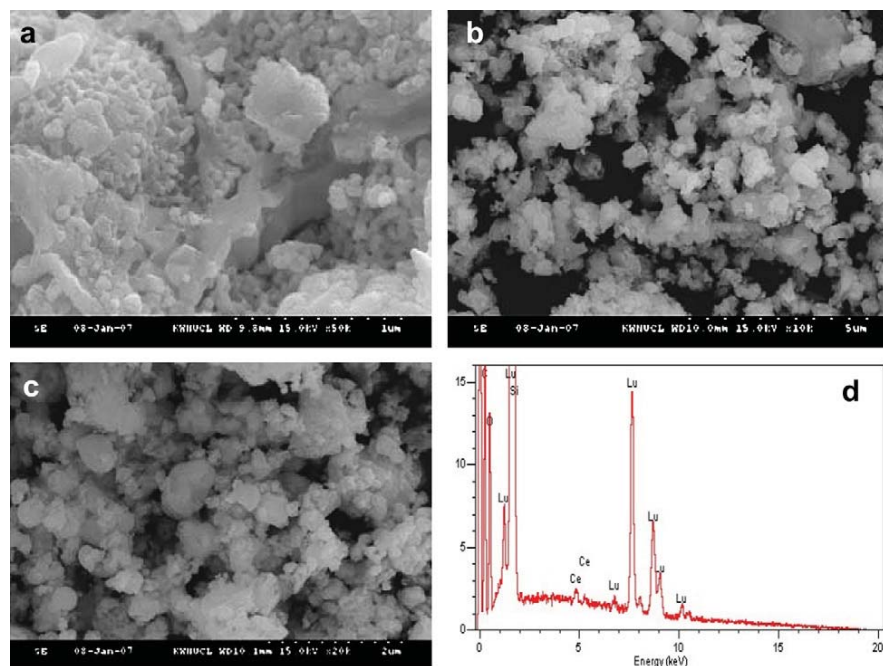


Fig. 3. SEM micrographs of (a) Lu_2SiO_5 , (b) $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}0.01\%$, (c) $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}0.03\%$, and (d) EDS spectra for S3 heated at 1200 °C.

The excitation spectra and emission spectra of $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ powders were obtained in different concentrations of Ce^{3+} (=0, 0.01 and 0.03). Fig. 4 shows the excitation spectra of $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ powders at the emission wavelength of 380 nm. The excitation spectra of $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ powders show two broad bands at 306 and 350 nm, which are assigned to the Ce^{3+} ion transitioning from the 5d level to the 4f ground states.

Fig. 5 shows emission spectra of $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ powders at the excitation wavelength of 356 nm. Lu_2SiO_5 powder itself is not scintillate, but scintillation yield is higher in $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ powder. Emission intensity increases at a cerium doping of 0.01%, but decreases at 0.03%. A very broad spectra were observed in the range of 350–530 nm, and the broad wavelength band on the right side of the spectra should be ascribed to the same 5d–4f transitions of Ce^{3+} as the case of $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ [7]. The concentration of Ce^{3+} ions has not yet been optimized in the sol–gel route.

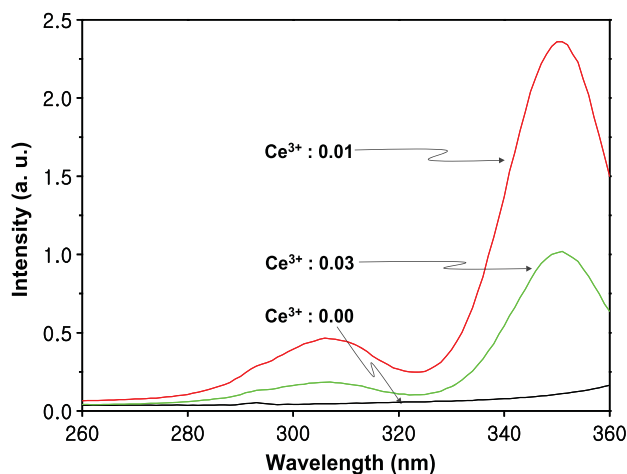


Fig. 4. Excitation spectra of Lu_2SiO_5 and $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ powders heated at 1200 °C.

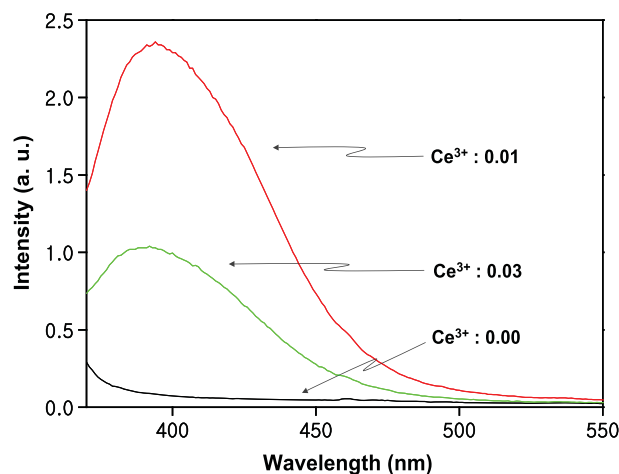


Fig. 5. Emission spectra of Lu_2SiO_5 and $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ powders heated at 1200 °C.

4. Conclusion

Cerium doped lutetium silicate powders were prepared by sol–gel process with different cerium concentrations (0, 0.01 and 0.03 mol%). The crystallization of lutetium silicate are observed at 1.073 °C in S2 (and S3:1.058 °C) sample. The formation of lutetium silicate phases was confirmed by XRD analysis for the powders heated at 1200 °C, of which mixed phases containing Lu_2SiO_5 and $\text{Lu}_2\text{Si}_2\text{O}_7$ phase were observed. Lu_2SiO_5 phase is formed more in 0.01 mol% than in the doping of 0.03 mol%. Lutetium silicate powder was homogeneous and constituted of small spherical particles of about 400 nm. Lutetium silicate powder itself is not scintillate, but $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ powder exhibits the higher scintillation yield. Very broad spectra were observed in the range of 350–530 nm, and emission intensity increases at a Ce doping of 0.01%, but decreases at 0.03%.

References

- [1] A.H. Gomes de Mesquita, A. Buil, *J. Electrochem. Soc.* 116 (6) (1969) 871.
- [2] C.L. Melcher, J.S. Schweitzer, *IEEE Trans. Nucl. Sci.* 39 (4) (1992) 502.
- [3] C.L. Melcher, US Patent 4,958,080 (1990) and 5,025,151(1991).
- [4] M. Kapusta, et al., *IEEE Trans. Nucl. Sci.* NS-47 (2000) 1341.
- [5] C.D. Brandle, A.J. Valentino, G.W. Berkstresser, *J. Cryst. Growth* 79 (1989) 308.
- [6] J.M. Nedelec, D. Avignant, R. Mahiou, *Chem. Mater.* 14 (2002) 651.
- [7] C. Mansuy, R. Mahiou, J.M. Nedelec, *Chem. Mater.* 15 (2003) 3242.
- [8] C. Mansuy, J.M. Nedelec, C. Dujardin, R. Mahiou, *J. Sol–gel Sci. Technol.* 32 (2004) 253.
- [9] E. Bescher, S.R. Robson, J.D. Mackenzie, B. Patt, J. Iwanczyk, E.J. Hoffman, *J. Sol–gel Sci. Technol.* 19 (2000) 325.
- [10] Guohao Ren, Laishun Qin, Sheng Lu, Huanying Li, *Nucl. Instrum. Meth. A* 531 (2004) 560.
- [11] Kirk Lennstrom, Steven J. Limmer, Guozhong Cao, *Thin Solid Films* 434 (2003) 55.
- [12] H. Shang, Y. Wang, B. Milbrath, M. Bliss, G. Cao, *J. Lumin.* 121 (2006) 527.
- [13] Lempicki, et al., US patent 6,967,330 (2005).