J Mater Sci (2008) 43:2213–2216
DOI 10.1007/s10853-007-2112-x

NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Synthesis of $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ phosphor by hydrothermal Si alkoxide gelation

**Yoshihito Suzuki · Masato Kakihana ·
Yasuo Shimomura · Naoto Kijima**

Received: 27 November 2006 / Accepted: 13 August 2007 / Published online: 22 December 2007

Abstract Single-phase $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ green emission phosphor was synthesized by the hydrothermal silicon alkoxide gelation method. Such specimens demonstrated higher emission intensity than the $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ samples that are prepared by conventional solid-state reaction method. It was also demonstrated that annealing in the presence of graphite as an oxygen scavenger significantly improves the fluorescence properties of this material.

Introduction

$Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ is a green emission phosphor, which can be excited by blue light [1, 2]. The fluorescence process involves electronic transition between $4f^15d^0$ and $4f^05d^1$ states of Ce^{3+} ion. The emission wavelength depends on the energy of the $4f^05d^1$ state which is very sensitive to the coordination environment of Ce^{3+} due to the crystal field splitting. Few crystals allow such energy of the $4f^05d^1$-level that Ce^{3+} can absorb visible light. It has been known that scandium favors considerable reduction of Ce^{3+} $4f^05d^1$ energy [3] and therefore one may expect that it improves absorption of visible light by Ce^{3+} ion in $Ca_3Sc_2Si_3O_{12}$, although full details of this phenomenon have not been understood yet.

Thus, it is expected that a Sc-containing silicate, such as $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ material may find its application as the green component of a white-lamp based on downconversion of blue light of LED excitation. Although the use of single-phase $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ results in an increase in the materials fluorescence intensity, it is difficult to obtain because, Sc_2O_3, one of its main components, has low chemical reactivity and remains in the mixture as an unreacted impurity. Hence, we attempted to develop a new method of producing single-phase $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$.

Decreasing the particle size of the starting materials is an effective method of increasing reaction speed. The most efficient approach relies on atomic-scale mixing in the liquid phase with application of advanced solution methods, such as the sol–gel technique [4, 5]. Sol–gel transformation takes place during metal alkoxide hydrolysis, but in the system under discussion, Si alkoxide has a very low hydrolysis rate compared to Ca, Sc and Ce alkoxides, and thus the gel precursor will be inhomogeneous, particularly with respect to Si. Another solution method—the polymerized complex method [6, 7]—is based on polyester formation between metal-citric acid complexes and propylene glycol. However, as soluble silicon compounds are rare and the most suitable Si alkoxide is poorly soluble in a glycol and rather volatile at the temperatures required for the polyeserification reaction, a solid SiO_2 colloidal suspension must be used, as a starting material. In this case, the particle size of SiO_2 determines the limit of homogeneity, and atomic-scale mixing becomes difficult to achieve.

Another possibility is the hydrothermal gelation method (HTG method), in which, the mixing of dissolved metal

Y. Suzuki · M. Kakihana (✉)
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
e-mail: kakihana@tagen.tohoku.ac.jp

Y. Shimomura · N. Kijima
Research and Technology Development Division, Mitsubishi Chemical Group Science and Technology Research Center, Inc., 1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan

species is carried out in the liquid phase with the growing silica polymeric network to form a homogeneous precursor. This method relies on the formation of a gel network during hydrolysis of Si alkoxide in the course of a hydrothermal reaction. If other metal ions are present in the solution, these ions become involved in the Si–O gel network, and solution homogeneity is preserved. The important feature of this method is that in the closed system silicon alkoxide evaporation is prevented, while hydrothermal conditions accelerate hydrolysis of the alkoxide.

A sample obtained by the HTG method using Si alkoxide and aqueous solutions of Ca, Sc and Ce was single-phase and did not contain the usual impurity phase of Sc_2O_3. The fluorescence intensity of the sample was more than twice that of samples prepared by the solid-state reaction method (SSR). Thus, it was confirmed that HTG is effective for the synthesis of single-phase high-brightness $Ca_3Sc_2Si_3O_{12}$:Ce^{3+} phosphor material.

Experimental

The samples in this work were prepared by the HTG method and conventional solid-state reaction method. For HTG synthesis, starting materials were $Ca(NO_3)_2 \cdot 4H_2O$ (high grade, Kanto Kagaku, Japan), $Ce(NO_3)_3 \cdot 6H_2O$, Sc_2O_3 (99.99%, Nippon Yttrium Co., Ltd., Japan), tetraethoxysilane (TEOS) (95%, Kanto Kagaku, Japan), nitric acid (61%, Kanto Kagaku, Japan). $Ca(NO_3)_2$ and $Ce(NO_3)_3$ were dissolved in distilled water, and Sc_2O_3 was dissolved in nitric acid. All solutions were mixed together with TEOS in a volume ratio which corresponded to a molar ratio of Ca:Ce:Sc:Si = 2.97:0.03:2.00:3:00. The solution was put into an autoclave, which was then sealed, placed in an oven (ANS-111S, Isuzu, Japan) and heated to 200 °C for 24 h. After this hydrothermal treatment, the resulting gel had been transferred from the vessel into a cone flask, which was then covered with a lid. This flask was kept in a dry oven at 120 °C until all the water had evaporated, and was then placed in a mantle heater (MS-20, Omtop, Japan) and heated to 500 °C to remove organic residues. This process was used to obtain the precursor, which was later subjected to heat-treatment in order to form the phosphor material. A reference sample was prepared by SSR synthesis. Starting materials were $CaCO_3$ (high grade, Kanto Kagaku, Japan), $Ce(CH_3COO)_3$ (Kanto Kagaku, Japan), Sc_2O_3 (99.99%, Nippon Yttrium Co., Ltd., Japan), and SiO_2 (70 nm, Wako, Japan). The reagents were mixed in an agate mortar in the same molar ratio as for the HTG method to form a powder mixture (SSR precursor).

Both precursors were heat-treated in an electric furnace (KDF75) at 800 °C and 20 Pa pressure to cause decomposition of carbonates. After this process, the products were heat-treated in air at 1,400 °C for 2 h in the electric furnace (KDF-314N, Koyo, Japan). Additional sample was prepared from the HTG precursor in the reducing atmosphere. In this experiment a crucible with the sample was placed into a larger crucible containing graphite powder, which was covered by a lid and heat treated at 1400 °C for 2 h. The final products were analyzed by XRD phase analysis (RINT2000, Rigaku, Japan) using CuKα radiation. Particles morphology were examined by scanning electron microscope (SEM) (LEO982, Carl Zeiss, Germany) operated at 3 kV. Emission spectra were acquired by the fluorescence spectrometer (F4500, Hitachi, Japan) using 447 nm light for the excitation.

Results and discussions.

Figure 1 shows XRD patterns of the samples obtained by conventional solid-state reaction and by the HTG method. Each diffraction peak originating from the target compound, $Ca_3Sc_2Si_3O_{12}$, is indicated by a white circle; black squares represent the impurity Sc_2O_3. It can be seen in Fig. 1a that the SSR product is a multiphase sample

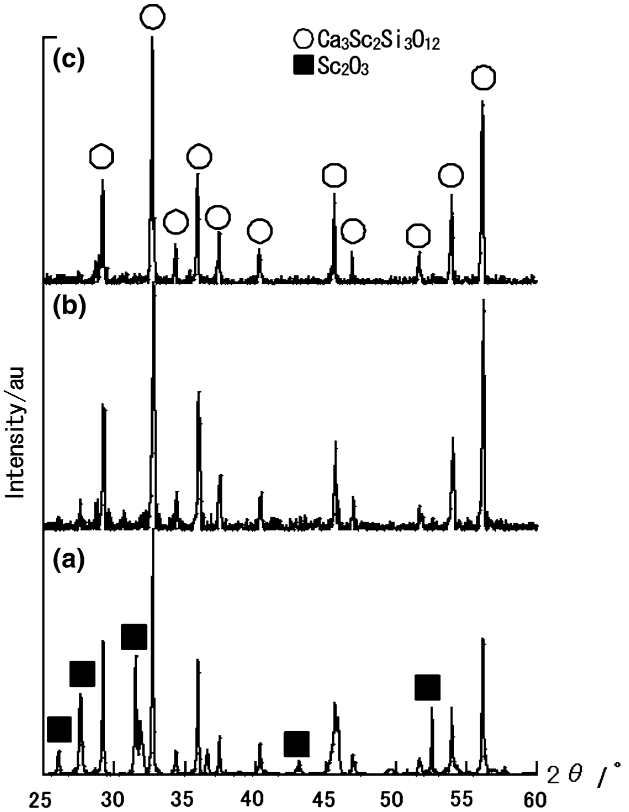

Fig. 1 Powder XRD patterns of $Ca_3Sc_2Si_3O_{12}$:Ce material prepared by solid-state reaction method in air (**a**), the hydrothermal gelation method in air (**b**) and by the hydrothermal gelation method in the reducing atmosphere created by graphite (**c**)

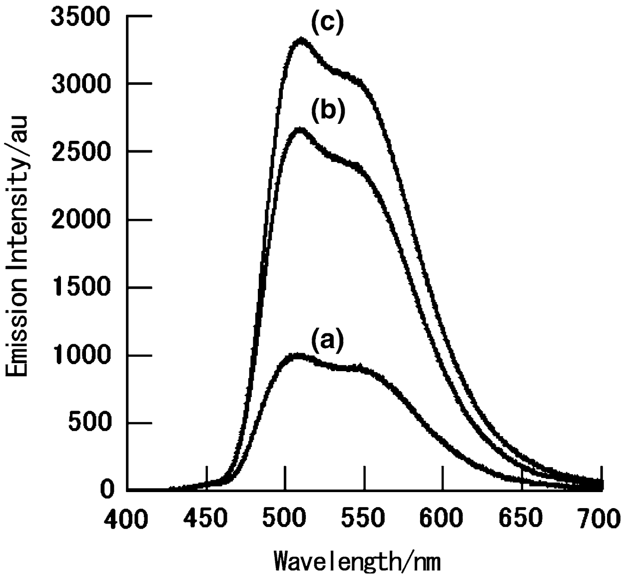

Fig. 2 Fluorescence emission spectra of $Ca_3Sc_2Si_3O_{12}$:Ce samples prepared by solid-state reaction method in air (**a**), the hydrothermal gelation method in air (**b**) and by the hydrothermal gelation method in the reducing atmosphere created by graphite (**c**). Excitation light wavelength is 447 nm

consisting of $Ca_3Sc_2Si_3O_{12}$ and Sc_2O_3, while the HTG product consists of single-phase $Ca_3Sc_2Si_3O_{12}$ (Fig. 1b, c).

Figure 2 shows fluorescence spectra of the samples excited by 447 nm light. The spectra of the SSR and HTG samples heat-treated in air and the HTG sample prepared in the presence of graphite are presented by curves (a), (b) and (c) respectively. The shape of each emission spectrum is the same, with a maximum at around 510 nm, but the intensities are different. The intensity of the HTG sample annealed in air (Fig. 2b) was 2.5 times greater, and that of the HTG sample heat treated in the reducing atmosphere (Fig. 2c) three times greater, than the reference SSR sample.

Figure 3 shows SEM micrographs of two samples. One may conclude from Fig. 3a and b that SSR sample is composed of densely sintered grains aggregated into a larger particles of 20–100 μm size. Each grain has poorly defined habitus, which can be an indication of a liquid phase formation during the synthesis. The HTG method seems to have a tendency to form bigger aggregates of around 200–500 μm in size (Fig. 3c). However, their internal structure revealed at higher magnification (Fig. 3d) shows presence of grains with well-defined morphology and probably much better crystallinity compared to SSR sample.

It can be concluded that the solution method is very efficient for synthesis of the single-phase $Ca_3Sc_2Si_3O_{12}$:Ce phosphor. This is due to the higher reactivity of the homogeneous precursor resulting from atomic-scale mixing. This high reactivity results in an increase in the ratio of the target compound $Ca_3Sc_2Si_3O_{12}$ to unreacted Sc_2O_3. It also results in high crystallinity, better grain morphology and greater fluorescence intensity. The heat treatment in the presence of graphite yielded a sample with even higher fluorescence intensity than that of the sample treated in air. This was due to the increased concentration of fluorescence-active Ce^{3+} ions resulting from reduction by CO gas formed from graphite [8, 9]. The concentration of Ce^{3+} and Ce^{4+} ions in the final $Ca_3Sc_2Si_3O_{12}$ material is determined by oxygen fugacity. In other words, it depends on the oxygen partial pressure and synthesis temperature. Use of graphite as an oxygen scavenger allows shifting the equilibrium toward higher concentration of Ce^{3+}. It is

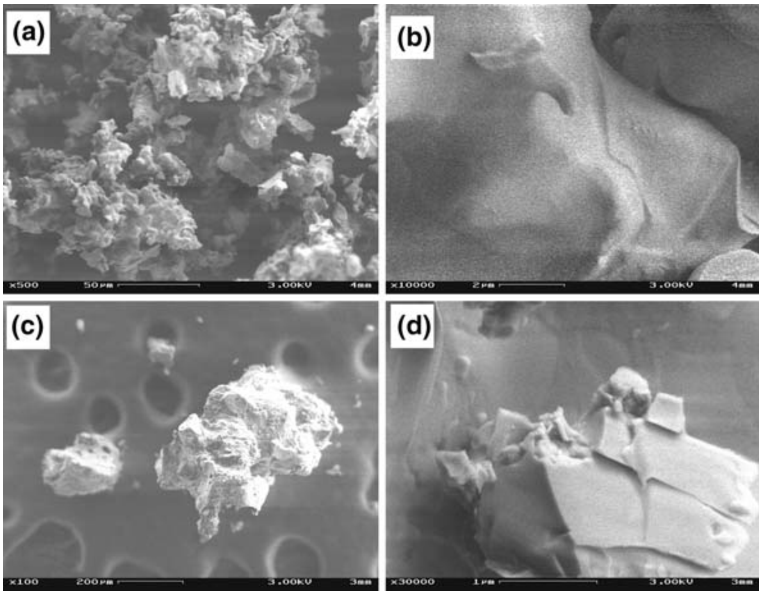

Fig. 3 SEM micrographs of $Ca_3Sc_2Si_3O_{12}$:Ce powders prepared by solid-state reaction method in air at ×500 (**a**), ×10,000 (**b**) magnifications and by the hydrothermal gelation method in air at ×300 (**c**) and ×30,000 (**d**) magnifications

interesting if one can enhance the fluorescence intensity further by use of a stronger reducing agent. At the current stage we are unable to provide the unambiguous answer for this question because synthesis of $Ca_3Sc_2Si_3O_{12}$:Ce in the more reducing atmosphere often results in the partial reduction of SiO_2. Thus careful optimizations of synthesis conditions for this green emission phosphor are currently under way.

Conclusion

Single-phase $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ was produced by the HTG method. The fluorescence intensities of samples prepared by this method were more than twice as strong as those of samples prepared using a solid-state reaction. Samples obtained by heat treatment in the presence of graphite showed higher intensity by about 24% than samples annealed in air. The reason for the successful preparation of the single-phase $Ca_3Sc_2Si_3O_{12}$:Ce green phosphor is the formation of a uniform precursor in which homogeneity achieved in the solution is preserved by Si–O gel network. The HTG method is a promising tool for the synthesis of silicates containing components with low reactivity.

Acknowledgements This work was supported by Grant in Aid for Scientific Research 16080206 provided by Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

1. Novak GA, Gibbs GV (1971) Am Mineral 56:791
2. Shimomura Y, Kijima N (2004) U.S. Pat. Appl. 2004/0251809A1
3. Dorenbos P (2002) J Lumin 99:283
4. Colomban Ph (1989) Ceram Int 15:23
5. Chatterjee M, Naskar MK (2006) Ceram Int 32:623
6. Fujimori H, Yahata D, Yamaguchi N, Ikeda D, Ioku K, Goto S (2001) J Ceram Soc Jap 109:391
7. Kakihana M (1996) J Sol–Gel Sci Technol 6:7
8. Zhang XY, Liu QS, Lu LP, Wang XC, Bai ZH (2005) Chin J Inorg Chem 21:665
9. Shin SH, Jeon DY, Suh KS (2001) Jap J Appl Phys Part-1 40:4715