Journal of the Ceramic Society of Japan 117 [3] 313-315 2009 **Paper**

Synthesis of $Zn_2SiO_4:Mn^{2+}$ green emission phosphor by hydrothermal gelation method using a novel water soluble silicon compound

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Recently our research group has developed a new water-soluble silicon compound. In current work this compound was employed as a starting reagent for synthesis of $Zn_2SiO_4:Mn^{2+}$ green emission phosphor by the hydrothermally induced gelation (HTG) method and by the polymerizable complex (PC) method. The sample obtained by the HTG method was composed of $Zn_2SiO_4:Mn^{2+}$ single phase and showed two times higher emission intensity than a reference sample synthesized by the conventional solid-state reaction method.

Key-words : Water-soluble silicon compound, Zinc silicate, Phosphor, Hydrothermal gelation method, Water solution method

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1. Introduction

Silicon is one of the very important basic elements constituting various functional materials. Reagents containing silicon are excessively consumed in many applied fields, such as zeolite- and glass-industries as well as in the field of ceramics.[1] Therefore, in the view of the current energy and environmental safety concerns development of manufacturing methods for silicon-containing materials that are characterized by low environmental impact is strongly desired by the industry. The aqueous solution based processes are known to provide homogeneous mixing of starting materials on the atomic level, and by optimizing processing conditions, future development of the aqueous solution technologies can be expected, which will include the following advantages: (1) high performance functional ceramics with precisely controlled compositions can be synthesized and (2) processes with low environmental impact can be designed using water as a processing solvent. Nevertheless, silicon compounds soluble in pure water have remained virtually unknown until now, and therefore it was difficult to apply aqueous solution based methods for synthesis of silicon-containing ceramics. Conventional compounds such as SiO_2 and tetraethoxysilane (TEOS), which have been used as raw materials for the synthesis of silicon-containing ceramics up to now,[2),3)] are insoluble in water, and they were inappropriate Si-sources in combination with an aqueous solution process. Recently, the present authors have developed the new unique water soluble silicon compound (WSS), which can be the powerful alternative for conventional silicon reagents. Thus the convenient synthesis route for silicon-containing high performance functional ceramics based on the aqueous solution process using WSS has emerged from now.

In this study, synthesis of zinc silicate green phosphor $Zn_2SiO_4:Mn^{2+}$ [4)] was attempted by employing WSS as a Si-source in the hydrothermally induced gelation (HTG) method, which is a variation of aqueous solution techniques.[5)] To reveal the potential of WSS as a silicon-containing precursor for an aqueous solution process, a series of $Zn_2SiO_4:Mn^{2+}$ samples have been prepared by solid state reaction, polymerizable complex (PC) method[6),7)] using WSS and by HTG method employing TEOS as a Si-source. Then phase compositions and fluorescence properties of the synthesized materials were compared.

2. Experimental

2.1 Preparation of water soluble silicon compound (WSS)

Tetraethoxysilane (TEOS) (99.9%, Kanto Chemical Co., Inc.) and propylene glycol (PG) (99.0%, Kanto Chemical Co., Inc.) were mixed (molar ratio = 1:4) in a conical flask. At this point, TEOS and PG formed a two-phase liquid system. This mixture was heated to 80°C and kept at this temperature for 48 h with constant stirring to proceed the substitution reaction between ethoxy group of TEOS and PG. After that, 100 μl of hydrochloric acid (35.0%, Kanto Chemical Co., Inc.) was added to the immiscible mixture, which led to complete mixing between the two liquid phases almost instantaneously. The prepared solution was diluted with distilled water to adjust silicon concentration to 1.0 mol/L. This stock solution containing silicon was used as a starting reagent for synthesis of $Zn_2SiO_4:Mn^{2+}$ (chemical formula - $Zn_{1.98}Mn_{0.02}SiO_4$) by variety of solution methods. Synthesis procedures are schematically explained in **Fig. 1**.

2.2 Hydrothermally induced gelation method

Starting materials were 1.0 mol/L stock solution of WSS or TEOS, $Zn(CH_3COO)_2$ (99.0%, Kanto Chemical Co., Inc.) and $MnCl_2$ (99.0%, Kanto Chemical Co., Inc.) aqueous solutions. The reagents in the desired ratio were put into an autoclave, and heated at 200°C for 24 h in an oven (ANS–111S, Isuzu) to promote the hydrolysis of WSS resulting in formation of siloxane bond network, in which other ions were incorporated homogeneously. The obtained gel was dried at 150°C for 2 h in a mantle heater (GBRT–5H, Taika Denki K. K.) and the resultant powder

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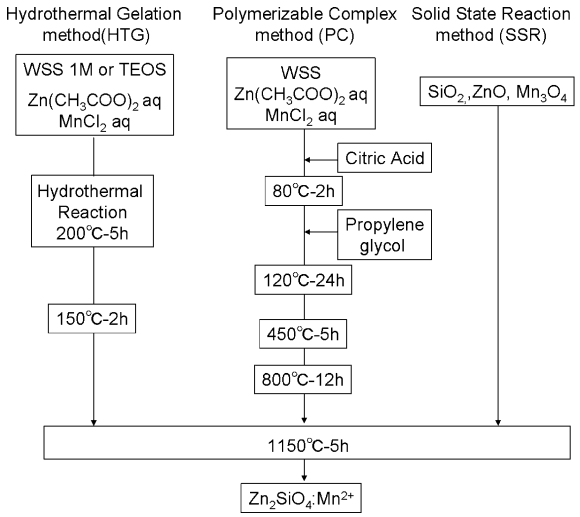

Fig. 1. Flowchart of $Zn_2SiO_4:Mn^{2+}$ synthesis by hydrothermally induced gelation method, polymerizable complex method and solid state reaction method.

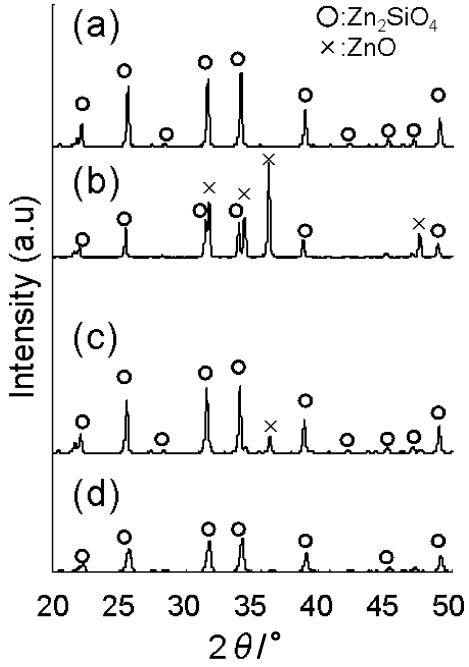

Fig. 2. XRD patterns of $Zn_2SiO_4:Mn^{2+}$ samples (a) prepared by hydrothermally induced gelation method (HTG) using water soluble silicon compound (WSS) or (b) tetraethoxysilane (TEOS) as silicon reagents, (c) by polymerizable complex method (PCM) and (d) solid state reaction method.

was heat-treated at 1150°C for 5 h in a box furnace (KBF314N1, Koyo Thermo Systems Co., Ltd.) in the air to obtain $Zn_{1.98}Mn_{0.02}SiO_4$ material.

2.3 Polymerizable complex method

Stoichiometric quantities of 1.0 mol/L WSS stock solution, $Zn(CH_3COO)_2$ and $MnCl_2$ aqueous solutions were mixed together, followed by addition of citric acid (CA: 98.0%, Wako Pure Chemical Ind., Ltd.) with the molar ratio of [All metals]:[CA] = 1:4. This aqueous solution was kept at 80°C for 2 h with stirring. After that, propylene glycol (PG: 99.0%, Kanto Chemical Co., Inc.) was introduced with the molar ratio of [All metals] : [PG] = 1:20; the temperature of the solution was increased to 120°C, and it was kept at this temperature for 24 h with continuous stirring. Under this condition polyesterification reaction between CA and PG took place, and metals species homogeneously distributed in the solution became bound to the polymeric network. The resulting polymeric gel was placed into a mantle heater for pyrolysis at 450°C. Then oxidation of carbon containing species was accomplished by heat treatment at 800°C in a box furnace. Final heat-treatment of the resultant precursor was carried out at 1150°C for 5 h in the same way as that mentioned above.

2.4 Solid state reaction method

SiO_2 (70 nm, Wako Pure Chemical Ind., Ltd.), ZnO (99.0%, Kanto Chemical Co., Inc.), and Mn_3O_4 (99.9%, Kojundo Chemical Lab. Co.,Ltd.) as starting materials were mixed in an agate mortar in the required stoichiometry corresponding to $Zn_{1.98}Mn_{0.02}SiO_4$ composition. This mixed powder was heat treated at 1150°C for 5 h to obtain the target material.

All prepared samples were subjected to XRD phase analysis (RINT 2000, Rigaku Co.). Particles morphology was examined by means of scanning electron microscope (LEO 982, Carl Zeiss Inc., Germany). Excitation and emission spectra were measured by means of a fluorescence spectrometer (F4500, Hitachi, Ltd.).

3. Results and discussion

Figure 2 presents XRD patterns of samples synthesized by HTG method employing WSS or TEOS as starting reagents, by PC method using WSS and by SSR method. One can conclude from Fig. 2 that the sample prepared by HTG method using WSS as a source of silicon was composed of single-phase $Zn_2SiO_4:Mn^{2+}$ with good crystallinity. The material prepared by SSR was also phase pure; however intensities of the XRD peaks were lower than in the case of HTG method, suggesting poor crystallinity. The other samples prepared by PC method or when TEOS was used as a silicon source had good crystallinity, but contained considerable amounts of ZnO impurity phase. The amount of impurity phase was especially significant when TEOS was used as a reagent in HTG method, which is not surprising since TEOS is poorly soluble in water and it was impossible to achieve uniform mixing of components during the hydrothermal treatment. The reason why ZnO formed as an impurity In the case of the PC method could be explained in terms of a possible phenomenon that WSS can be vaporized during the heating process at 80°C or 120°C.

Figure 3 shows luminescence spectra of the samples prepared by different methods. Emission of the phosphors prepared by HTG method from WSS was the strongest, and it was approximately two times higher than emission from the material prepared by SSR method. The considerable improvement of the emission intensity found for this sample is related to the single phase nature of the powder, and it indicated that Mn^{2+} activator ions were distributed very homogeneously in the Zn_2SiO_4 matrix. Formation of the uniform white gel in HTG method after hydrothermal treatment also suggests that high homogeneity on the atomic level achieved in the solution was preserved. The sample synthesized by PC method exhibited slightly lower emission probably due to the presence of the ZnO secondary phase (see Fig. 2). Especially week emission intensity was observed from the specimen prepared by HTG method when TEOS was applied as a silicon precursor and it should be regarded as a consequence

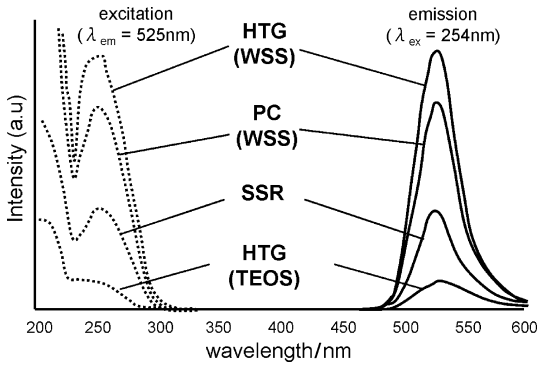

Fig. 3. Emission and excitation spectra of $Zn_2SiO_4:Mn^{2+}$ samples prepared by hydrothermally induced gelation method (HTG) using water soluble silicon compound (WSS) or tetraethoxysilane (TEOS) as silicon reagents, by polymerizable complex method (PCM) and solid state reaction method.

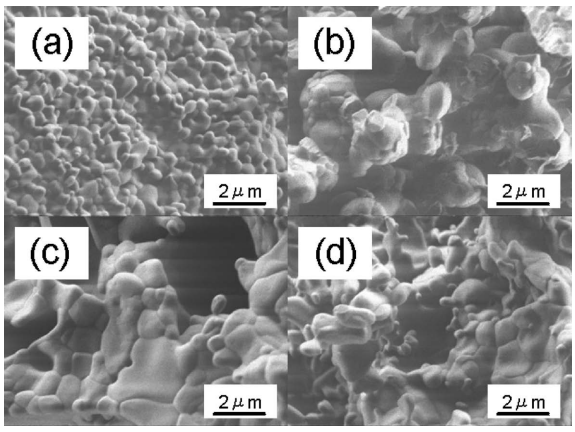

Fig. 4. SEM micrographs of $Zn_2SiO_4:Mn^{2+}$ samples (a) prepared by hydrothermally induced gelation method (HTG) using water soluble silicon compound (WSS) or (b) tetraethoxysilane (TEOS) as silicon reagents, (c) by polymerizable complex method and (d) solid state reaction method.

of extreme inhomogeneity due to the phase separation between aqueous solution and TEOS.

SEM micrographs of the prepared samples are presented in **Fig. 4**. One may notice from comparing Fig. 4(a) with the rest of the SEM images that microstructure of the material prepared from WSS by HTG is quite different from those of the other samples. The powder prepared from the new water soluble silicon compound is composed of densely sintered submicron particles having a relatively small variation in size or shape. In contrast, the $Zn_2SiO_4:Mn^{2+}$ phosphors synthesized by PC method, SSR method or HTG method when TEOS was used as a silicon source are characterized by more irregular morphology, which are composed of bulky particles with the dimensions ranging from 1 μm to 5 μm. Such a regular microstructure of the HTG (WSS) sample as it is displayed in Fig. 4 may be additional evidence of higher uniformity of this type of precursor.

We calculated *R* factor (the amount of organic compounds required for synthesis of 1 g of target ceramics) for HTG and PC methods. This parameter allows for comparison of different synthetic methods with respect to their negative impact on the environment due to carbon dioxide emission. The expression shown below was used:

$$R\ \text{factor} = \frac{\text{Amount of organics required for synthesis (g)}}{\text{Amount of final material (g)}}$$

Table 1. Comparison of Phase Purity, Emission Intensity and *R* Factors Achieved in the Synthesis of $Zn_2SiO_4:Mn^{2+}$ Phosphor by Hydrothermal Gelation Method (HTG) Using Water Soluble Silicon Compound (WSS) or TEOS as Silicon Reagents, by Polymerizable Complex Method (PCM) and Solid State Reaction

	HTG (WSS)	HTG (TEOS)	PCM (WSS)	SSR (SiO_2)
Phase purity	○	×	×	△
Emission Intensity /HTG (WSS)	100	9.2	85.9	50.4
R factor	0.93	0.93	32.6	0

It turned out that *R* factor calculated for HTG method was 0.93, while for PC method it was 32.6. Thus, based on the *R* factor values one may conclude that potential environmental impact of HTG method when WSS is used as a silicon source was by the factor of ~30 lower than environmental impact of PC method. This result reflects the fact that in contrast to PC method, which utilized a lot of organic compounds as ligands and solvents, in the HTG method very little amounts of organic substances are used.

4. Conclusion

New water soluble silicon compound can be used as a convenient precursor for synthesis of silicon-containing phosphor material $Zn_2SiO_4:Mn^{2+}$ by hydrothermally induced gelation method using water as a process solvent. **Table 1** summarizes the results on phase purity, emission intensities and *R* factor values for the $Zn_2SiO_4:Mn^{2+}$ materials prepared in this work by four different synthesis methods. The sample prepared by HTG (WSS) method was superior to the other specimens in terms of all important characteristics. Namely it was possible to synthesize single-phase $Zn_2SiO_4:Mn^{2+}$ material with improved emission intensity, which was greater than for the materials prepared by conventional solid state reaction or by a traditional polymerizable complex method. Application of WSS as a precursor in combination with an aqueous solution based method produces rather low negative environmental impact during the synthesis, and it is possible to expect further applications of this silicon precursor for preparation of variety of silicon containing functional materials.

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