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Journal of the European Ceramic Society 31 (2011) 2629–2631
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Crystallization behaviour of neodymium doped yttrium silicate nanophosphors

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Available online 9 March 2011

Abstract

Sol–gel technique was used to prepare yttrium silicate powders doped with $0.01Nd^{3+}$. The crystallite sizes were determined to be 23 ± 0.5 nm from the XRD patterns of the powders annealed at 960 °C. The $Y_{4.67}(SiO_4)_3O$, $Y_2Si_2O_7$ and Y_2SiO_5 crystalline phases were observed upon heat treatment at 960 °C which is much lower than 1500–1650 °C are reported before.

Keywords: Yttrium silicate; Nanophosphors; Sol–gel processes

1. Introduction

Studies on the SiO_2–Y_2O_3 system exhibit interesting optical features. Some of the technical applications are the optical memory devices,[1] solid-state laser systems[2,3] and high energy phosphors.[4,5] The phase Diagram[6] of SiO_2–Y_2O_3 indicates two phase regions between 1:1 and 1:2 molar ratios in which Y_2SiO_5 and $Y_2Si_2O_7$ form a stable mixture. The yttrium orthosilicate (Y_2SiO_5) crystal has two different monoclinic structures: X_1 type (X_1-Y_2SiO_5) and X_2 type (X_2-Y_2SiO_5). The X_1 and X_2 types formed by varying the annealing temperature are known as crystallographic groups of $P2_1/c$, and B_2/b, respectively.[7] After annealing above 1190 °C, the crystal-structure changes from X_1 type to X_2 type.[8] The yttrium pyrosilicate ($Y_2Si_2O_7$) investigated from a structural point of view due to its complex high temperature polymorphism was reported for the first four forms[8]: $\alpha^{1225°C} \rightarrow \beta^{1445°C} \rightarrow \gamma^{1535°C} \rightarrow \delta$. In this stability range, these four modifications were synthesized from appropriate reagents using solid state reactions.[9]

We report the effects of molar concentrations of silica (TEOS) and yttrium on the phase separation and crystallization. Yttrium silicate phosphors doped with Nd^{3+} were synthesized by the sol gel technique and amorphous state was observed when the samples were annealed at 900 °C for 2 h. While the other studies report X_1-Y_2SiO_5 and α-$Y_2Si_2O_7$ forms at higher temperatures and larger sizes of nanocrystals, our results reveal smaller nanocrystalline sizes and $Y_{4.67}$ $(SiO_4)_3O$ phase at the 0.5- and 0.67-molar ratios of SiO_2 at 960 °C in addition to $Y_2Si_2O_7$ and Y_2SiO_5 phases.

2. Experimental

Samples were prepared in the SiO_2–Y_2O_3 binary systems using the $(100-x)SiO_2 + (x-1)Y_2O_3 + 1.0Nd^{3+}$ equation where x is 25, 35, and 45 corresponding to the samples labeled as SYN_{75}, SYN_{65}, and SYN_{55}, respectively. Precursors with the purity of 99.999% TEOS, 99.9% yttrium nitrate hexahydrate, and 99.9% neodymium acetate hydrate purchased from Sigma–Aldrich were used. Yttrium nitrate hexahydrate and neodymium acetate hydrate and TEOS were separately dissolved in double distilled water and ethanol. The yttrium nitrate and neodymium acetate solutions were mixed together at 70 °C under acidic conditions (1 N HNO_3) for 45 min and then left for cooling at room temperature. After the TEOS solution was added to the mixture and stirred for 2.5 h, the solution was placed unto circular petri dishes for three weeks to obtain a gel at room temperature. Some of the gels were annealed at 900 °C for 2 h, and some were annealed at 960 °C for three days. Subsequently, annealed samples reduced to powder were investigated for structural and morphological properties by XRD (SCHMADZU-XRD 6000) and SEM (Jeol JSM-6335F) at room

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doi:10.1016/j.jeurceramsoc.2011.02.013

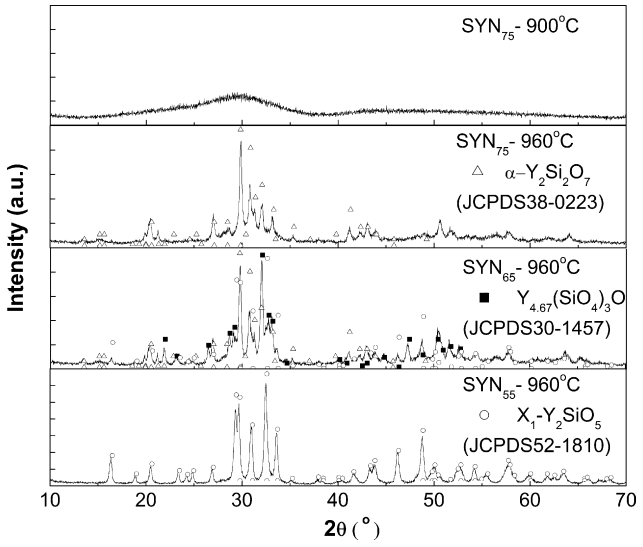

Fig. 1. The diffraction pattern of α-$Y_2Si_2O_7$ for SYN_{75}, α-$Y_2Si_2O_7$, $Y_{4.67}(SiO_4)_3O$ and X_1-Y_2SiO_5 for SYN_{65}, X_1-Y_2SiO_5 for SYN_{55} after annealing temperature.

temperature. TGA and DTA measurements of the gel-samples were made between 23 and 1400 °C.

3. Results and discussion

The TGA curves show a weight loss corresponding to the removal of surface water and residual organics below 480 °C. The DTA curves contain a glass temperature and a broad crystallization peak at around 980 °C and 1200 °C, respectively. These results agree well with those reported by Parmentier et al.[10] and Luo et al.[11]

We have also observed amorphous phases of the three powder-samples at 900 °C shown in Fig. 1. The diffraction patterns of α-$Y_2Si_2O_7$ for SYN_{75}, α-$Y_2Si_2O_7$, X_1-Y_2SiO_5, and $Y_{4.67}(SiO_4)_3O$ for SYN_{65}, and X_1-Y_2SiO_5 for SYN_{55} are illustrated. The SiO_2–Y_2O_3 phase Diagram[6] shows the crystal structures of $Y_2SiO_5 + Y_2Si_2O_7$ in the molar region of 50–67% from 1500 °C to 1650 °C. In our work, we observed the structures of α-$Y_2Si_2O_7$, $Y_{4.67}(SiO_4)_3O$ and X_1-Y_2SiO_5 for SYN_{65}, and X_1-Y_2SiO_5 for SYN_{55} at 960 °C in the same molar region. While $Y_2Si_2O_7 + SiO_2$ crystal structures were observed from 1500 °C to 1660 °C through the molar region of 67–100%, only the α-$Y_2Si_2O_7$, formed at 960 °C, is shown in Fig. 1.

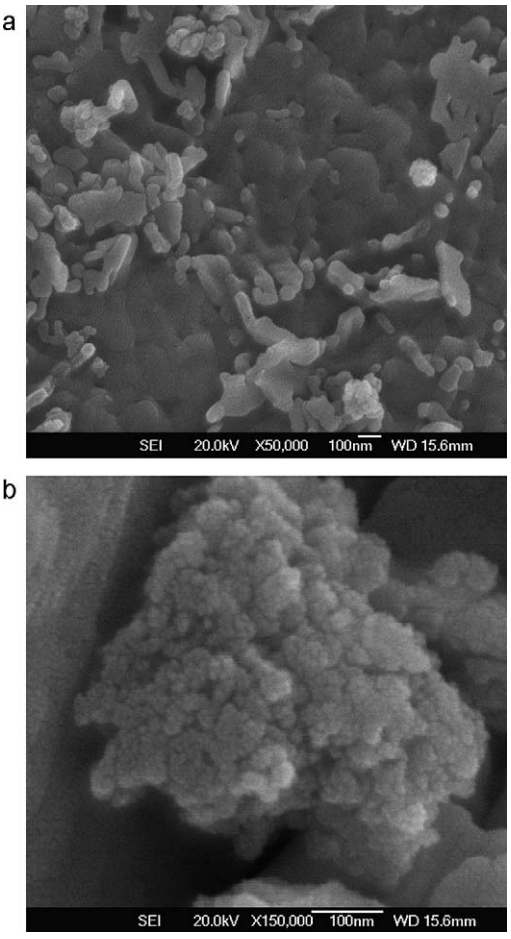

Fig. 3. (a) SEM image of SYN_{65} after annealing at 960 °C. (b) SEM image of SYN_{65} after annealing at 960 °C.

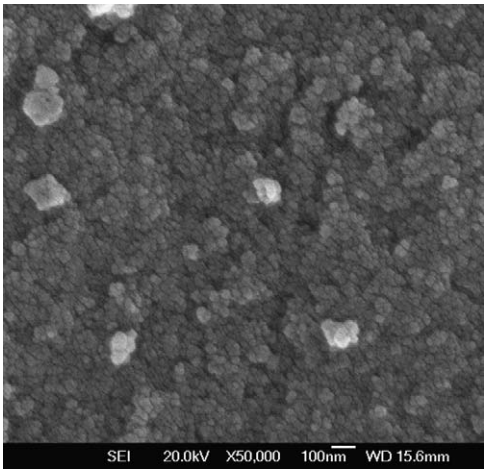

Fig. 2. SEM image of SYN_{75} after annealing at 960 °C.

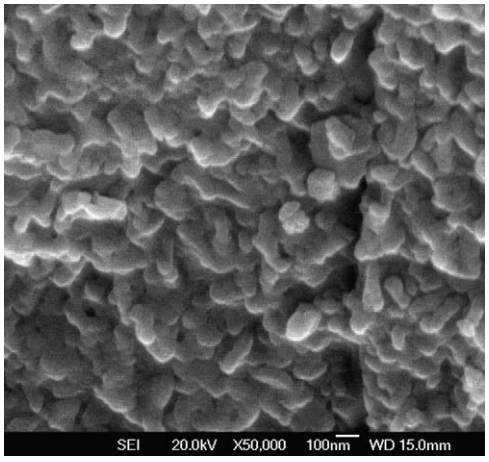

Fig. 4. SEM image of SYN_{55} after annealing at 960 °C.

The average crystalline sizes for all the three powder samples calculated from Scherrer's formula[12] are to be 23 ± 0.5 nm. The three powder samples annealed at 960 °C shown in Figs. 2–4 have irregular, agglomerated and narrow size shapes. The corresponding SEM and XRD results confirm each other. While one nano-structure was observed for a single phase in both powder samples of SYN_{75} and SYN_{55}, two different nano-structures were observed for three phases in SYN_{65}.

4. Conclusion

We successfully synthesized nanocrystalline yttrium silicates doped with neodymium using the sol–gel technique. We observed the existence of different crystal phases: X_1-Y_2SiO_5 phase for SYN_{55}, α-$Y_2Si_2O_7$ phase for SYN_{75}, and α-$Y_2Si_2O_7$, X_1-Y_2SiO_5, $Y_{4.67}(SiO_4)_3O$ phases for SYN_{65} are with the average nanocrystalline size of 23 ± 0.5 nm.

Acknowledgement

This work was supported by Science Institute of Marmara University with the project number FEN-C-DRP-090409-0079.

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