Effect of K$_3$PO$_4$ addition as sintering inhibitor during calcination of Y$_2$O$_3$ nanoparticles

K Soga$^{1,2}$, Y Okumura$^1$, K Tsuji$^1$ and N Venkatachalam$^2$

$^1$Department of Materials Science and Technology, Tokyo University of Science
2641 Yamazaki, Noda, Chiba 278-8510, Japan

$^2$Polyscale Technology Research Center, Tokyo University of Science
2641 Yamazaki, Noda, Chiba 278-8510, Japan

E-mail: mail@ksoga.com

Abstract. Erbium-doped yttrium oxide nanoparticle is one of the most important for fluorescence bioimaging under near infrared excitation. Particle size of it below 100 nm is an important requirement for a cellular bioimaging. However, the synthesis with such small particles is difficult at the calcination temperature above 1200 °C due to the sintering and crystal growth of the particles. In this study, yttrium oxide nanoparticles with average size of 30 nm were successfully synthesized by using K$_3$PO$_4$ as a sintering inhibitor during the calcination. A single phase of cubic Y$_2$O$_3$ as the resultant material was confirmed by XRD, which was also confirmed to emit a bright upconversion emission under 980-nm excitation. Improvement of chemical durability due to the introduction of phosphate group on the surface of the Y$_2$O$_3$ particles is also reported.

1. Introduction
Fluorescence bioimaging is one of the most important tools for biological researches and medical diagnosis to visualize biological phenomena. Current problems for the fluorescence bioimaging are color fading of the imaging probes, photonic damage to the biological substances, auto fluorescence and strong scattering due to the use of short-wavelength light such as ultra violet light as an excitation light. The authors have developed fluorescence bioimaging system that can be excited by near infrared (NIR) light by using ceramic nanophosphors as fluorescence probes [1, 2]. Rare-earth-doped ceramic nanophosphors (RED-CNP) have developed as NIR bioimaging probes. Yttrium oxide (Y$_2$O$_3$) nanoparticles doped with erbium (Er) is one of the best candidates because nanoparticles are available by various precursor precipitation routs and they can both emit visible upconversion (UC) emission in visible wavelength region and NIR emission around 1500-nm wavelength region [3-13].

An important requirement to the RED-CNP to be used for the bioimaging is sizes between 10 and 200 nm [1] to keep both of the emission intensities and the dispersion in physiological conditions. Various methods to prepare Y$_2$O$_3$ particles with 20-200 nm size have been reported to date [3-13]. For the synthesis, calcination temperatures below 900 °C were essential to keep the particles un-sintered and un-grown from the controlled size of the precursors [13]. On the other hand, residual components such as hydroxyl or carbonate
groups are harmful to have an efficient emission from the material [14]. The removal of the residuals is still doubtful with the calcination temperature of 900 °C [15]. However, when increased with the calcination temperature above 900 °C, it should be difficult to keep the particles size to be less than 100 nm. It is required to have Y₂O₃ particles with a size less than 100 nm for the use of the particles as a imaging probe for an intra cell imaging.

The first objective of the present study is to decide a proper calcination temperature for achieving an efficient upconversion emission from Er³⁺-doped Y₂O₃ particles. Secondly, a use of K₃PO₄ as a sintering inhibitor to prevent the sintering between Y₂O₃ particles during the high temperature calcination at 1200 °C. Some extensional effects such as chemical durability improvement are also reported.

2. Experimental

2.1. Materials and sample preparation

Erbium nitrate pentagonal hydrate (Er(NO₃)₃ 5H₂O : purity 99.95%), yttrium nitrate hexagonal hydrate (Y(NO₃)₃ 6H₂O : purity 99.99%) and tri-potassium phosphate n-hydrate (K₃PO₄ nH₂O : purity 80%) were supplied from Kanto Chemical Company (Japan), sodium carbonate (Na₂CO₃ : purity 99%) were supplied from High Purity Chemical Laboratory Company (Japan).

For the experiments varying calcination temperature, hydroxide precursors were prepared by using a conventional alkaline co-precipitation method. The samples were calcined in air for 5 hrs at various temperatures between 800 and 1200 °C.

Er³⁺-doped Y₂O₃ nanoparticles were synthesized by calcining a hydroxyl carbonate precursor [5, 13]. In order to obtain the precursors, an aqueous solutions containing 200 ml of Er(NO₃)₃ (0.3 mmol/L) and Y(NO₃)₃ (4 mmol/L) were mixed into 200 ml of Na₂CO₃ (0.06 mol) aqueous solution and kept stirred for 0.5 hrs. The precipitation was washed by centrifugal washing for three times and dried at 80 °C overnight in air.

A fixed amount of Y(OH)CO₃ precursor was dispersed into various amount of K₃PO₄ aqueous solution with a fixed concentration so that molar ratio of Y: K₃PO₄ (denoted as 1:x in this paper) varies from 1:0 to 1:50. The mixture was maintained for 1 day at room temperature and dried by using a vacuum freeze dryer. The dried samples were calcined at 1200 °C for 5 hours and cooled in a furnace to room temperature. To remove K₃PO₄, particles were applied with centrifugal-wash until the pH reaches to 7 by distilled water and dried at 80 °C overnight in air.

2.2 Measurements

UC emission spectra were measured by using a spectrofluorometer (RF-5000, Shimadzu) under an excitation by IR diode laser at 980 nm. The resultant materials were supplied for XRD (XRD-6100, Shimadzu with Cu Kα radiation), FT-IR measurement (FT-IR8300, Shimadzu), SEM (S-4200, Hitachi) and TEM (LEO922, Carl Zeiss) imaging, which were performed by a . To test the chemical durability of the particles, 50 mg of the particles were at first dispersed into 50 mL NH₄OHaq with pH=7. The pH of the solution was measured after 1.0 M HCl aq. (0.2 mL) addition to make the initial solution pH to be 3.

3. Results and Discussion

Figure 1 shows the dependencies of UC emission intensity and infrared absorption due to hydroxyl groups on calcination temperatures. The values were obtained by integrating in corresponding regions in the UC emission and FT-IR spectra, respectively. By increasing the calcination temperature, the UC emission intensity increases and tends to saturate toward 1200 °C. Among the factors that control the UC emission intensity, the residual amount of the hydroxyl group affects on the upconversion intensity most seriously since the existence of the hydroxyl group heavily quenches the emission of the rare-earth ions due to the large vibration energy of the hydroxyl group (approx. 3400 cm⁻¹). The similar behaviors of the increase of the UC intensity and the decrease of the absorption due to the
hydroxyl group suggests that a calcination temperature above 1200 °C is required for an efficient emission from the RE-doped Y₂O₃ particles. On the other hand, it was found that the particle size of the particles calcined at 1200 °C was as large as several hundreds nm even when the calcination started from the precursors with several tens nm size.

To obtain the particles with the size less than 100 nm, sintering inhibition by introducing K₃PO₄ was performed. Figure 2 shows the XRD patterns of the calcined samples with or without K₃PO₄. It

**Figure 1.** Dependencies of UC emission intensity (closed circle) and infrared absorption due to hydroxyl groups (open square) on calcination temperatures.

**Figure 2.** XRD patterns of calcined samples together with JCPDS card data. x value in the figure denotes the molar ration of the K₃PO₄ to Y.
was found that the resultant particles are single phase cubic Y$_2$O$_3$ even in the case to calcine the precursor with 50 times larger molar amount of K$_3$PO$_4$ to Y. Figure 3 shows the UC emission spectra of Er in the samples calcined with or without K$_3$PO$_4$ under 980-nm excitation. The similarity of the spectra also supports that the resultant particles are in the same cubic Y$_2$O$_3$ as the samples without K$_3$PO$_4$ and not any of the compound contains phosphate groups.

Figure 4 shows the SEM images of the Y$_2$O$_3$ calcined with various amount of K$_3$PO$_4$. Without the addition of the K$_3$PO$_4$, the particles were sintered together to form a large agglomeration to form particles with sizes more than 1 μm. By increasing the amount of K$_3$PO$_4$, small particles with several tens nm size increased. When added with 50 times more molar ration of K$_3$PO$_4$ to Y, no large particle with a size more than 100 nm was found. The gradual increase of the small particles corresponds to the increase of K$_3$PO$_4$ is caused by the sintering inhibition effects by the K$_3$PO$_4$ among the precursor particles. According to the SEM and TEM observation of the resultant particles obtained by calcination with K$_3$PO$_4$ (x = 50) in Figure 5, the particle size ranged from 20 to 40 nm with an average

Figure 3. Upconversion emission spectra of the samples calcined without (a) or with (b) K$_3$PO$_4$ (x = 20).

Figure 4. SEM images of samples. The ratios in the pictures denote the molar ratios of the Y : K$_3$PO$_4$ (1 : x) during the calcination.
of 30 nm. Thus, we could successfully synthesized Y$_2$O$_3$ particles with size of several tens nm calcined at 1200 °C.

Figure 6 shows the FT-IR spectra of the Y$_2$O$_3$ particles calcined with or without K$_3$PO$_4$ inhibitor. Peaks round 1100 cm$^{-1}$ denoted as an arrow in the figure corresponds to the absorption due to PO$_4$ group. The absorption is only observed in the spectrum of the particles calcined with K$_3$PO$_4$ inhibitor. Along with the PO$_4$-absorption, characteristic peaks of a stretching mode hydroxyl group at 3400 cm$^{-1}$ and bending mode of water molecule around 1500 cm$^{-1}$ were observed only in the spectrum of the particles calcined with K$_3$PO$_4$ inhibitor. As a result of the XRD and UC emission experiments, the resultant particles are mostly crystalline Y$_2$O$_3$ while the FT-IR shows the existence of the PO$_4$ groups and water molecules together with the particles. Summarizing the whole results, the PO$_4$ groups exist on the surface of the Y$_2$O$_3$ particles with K$_3$PO$_4$ inhibitor. By the use of the K$_3$PO$_4$ inhibitor, chemical durability of the Y$_2$O$_3$ particles under acidic condition was improved well to be used under physiological conditions.

Figure 5. SEM (a) and TEM (b) images of a sample calcined with K$_3$PO$_4$ (x=50).

Figure 6. FT-IR spectra of the calcined samples without (a) or with (b) K$_3$PO$_4$ (x =20).
4. Conclusion

Required calcination temperature of Er-doped Y$_2$O$_3$ for efficient upconversion emission was found to be above 1200 °C, where the particle size under normal calcination grows up to be above 100 nm. By using K$_3$PO$_4$ as a sintering inhibitor, the particle size of the Y$_2$O$_3$ calcined at 1200 °C was successfully suppressed to be approximately 30 nm as average. The surface of the Y$_2$O$_3$ particles calcined with K$_3$PO$_4$ is covered with phosphate group, which improved the chemical durability of the particles under acidic conditions.

Acknowledgement

This work was supported by "Academic Frontier" Project for Private Universities: Matching Fund Subsidy from MEXT (Ministry of Education, Culture, Sports, Science and Technology), 2006-2010.

References

[1] Soga K, Tsuji T, Tashiro F, Chiba J, Oishi M, Yoshimoto K, Nagasaki Y, Kitano K and Mamaguchi S 2008 *J. Phys. Conf. Ser* 106 012023
[2] Konishi T, Shimizu M, Kameyama Y and Soga K 2007 *J. Mater. Sci. Mater. in Electron.* 18 S183
[3] Zako T, Nagata N, Terada N, Utsumi A, Sakono M, Yohda M, Ueda H, Soga K and Maeda N, *Biochem. Biophys. Res. Commun.* 2009 381 54
[4] Kamimura M, Miyamoto D, Saito Y, Soga K and Nagasaki Y 2008 *Trans. Mater. Res. Soc. Jpn.* 33 795
[5] Saito Y, Shimizu K, Kamimura M, Furusho H, Soga K and Nagasaki Y 2008 *Trans. Mater. Res. Soc. Jpn.* 33 803
[6] Matsuura D, Ikeuchi T and Soga K 2008 *J. Lumin.* 128 1267
[7] Konishi T, Shimizu K, Saito Y and Soga K 2007 *J. Photopolym. Sci. and Tech.* 20 11
[8] Konishi T, Yamada M, Soga K, Matsuura D and Nagasaki Y 2006 *J. Photopolym. Sci. and Tech.* 19 145
[9] Soga K, Koizumi R, Yamada M, Matsuura D and Nagasaki Y 2005 *J. Photopolym. Sci. and Tech.* 18 73
[10] Zako T, Nagata H, Terada N, Sakono M, Soga K and Maeda M 2008 *J. Mater. Sci.* 45 5325
[11] Kamimura M, Miyamoto D, Saito Y, Soga K and Nagasaki Y 2008 *J. Photopolym. Sci. and Tech.* 21 183
[12] Kamimura M, Miyamoto D, Saito Y, Soga K and Nagasaki Y 2008 *Langmuir* **24** 8864
[13] Venkatachalam N, Saito Y and Soga K, 2009 *J. Am. Ceram. Soc.* **92** 1006
[14] Soga K, Wenzhong W, Riman R E, Bryan J B and Mikeska K R 2003 *J. Appl. Phys.* **93** 2946
[15] Zhang J, Tang Z, Zhang Z, Fu W, Wang J and Lin Y 2002 *Mater. Sci. and Eng.* **A334** 246
[16] Pourbaix M, 1974 Atlas of Electrochemical Equilibria in Aqueous Solutions, NACE, Houston