Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 5067–5071

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Short communication

Molten salt synthesis of YAG:Ce^{3+} phosphors from oxide raw materials

Lin Gan[a,b], Zhi-Yong Mao[b,c], Fang-Fang Xu[a,*], Ying-Chun Zhu[c], Xue-Jian Liu[d]

[a]*State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China*
[b]*University of Chinese Academy of Sciences, Beijing 100049, PR China*
[c]*Inorganic Coating Materials Research Center, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China*
[d]*The Research Center of Structural Ceramic Engineering, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China*

Received 3 September 2013; received in revised form 12 September 2013; accepted 12 September 2013
Available online 18 September 2013

Abstract

In this study, we used oxides (Y_2O_3, CeO_2 and Al_2O_3) as the raw materials to fabricate YAG:Ce^{3+} phosphors by a molten salt synthesis (MSS) method. The formation of YAG phase strongly depends on the alumina source and firing temperature. Microstructure characterization indicates that “dissolution-precipitation” mechanism dominates the formation process of YAG in the alkali chlorides melt. Thus, highly active nano-Al_2O_3 starting powders promote their solution in the melt and guarantee a solute stoichiometric of YAG phase rather than other Y–Al–O compounds. The as-prepared YAG:Ce^{3+} phosphors show typical yellow emission peaked at 535 nm under excitation of 460 nm blue light, suggesting that MSS could be a promising method for the preparation of phosphor powders even though oxide raw materials are used.

Keywords: Phosphor; YAG:Ce^{3+}; Molten salt synthesis

---

1. Introduction

Yttrium aluminum garnet ($Y_3Al_5O_{12}$,YAG) has been intensely studied and widely used as a host for luminescent materials in the past decades because of its good chemical and thermal stability, high mechanical strength and excellent optical properties [1–2]. Recently, Ce^{3+}-doped $Y_{3-x}Ce_xAl_5O_{12}$ (YAG:Ce^{3+}) was exploited as an excellent phosphor applied in light-emitting diodes (LEDs) [3]. Solid-state reaction is the conventional method to synthesize YAG:Ce^{3+} phosphor, in which oxide raw materials are used. In order to achieve pure YAG phase without the two coexisting but undesired intermediate phases, $YAlO_3$ (YAP) and $Y_4Al_2O_9$ (YAM), the raw materials need to be mixed homogeneously and sintered at a high temperature (>1600 °C). Subsequently, time- and energy-consuming crushing and grinding processes are required to obtain desired particle size of the powders before further treatment [1,4]. However, these additional processes would introduce impurities and defects which result in considerable loss of emission efficiency of the phosphors.

In recent years, a series of wet chemical synthesis methods including sol–gel [4], co-precipitation [1,5], spray pyrolysis [6] and solvothermal [7] have been developed to synthesize YAG:Ce^{3+} phosphor powders at lower temperatures. However, these methods still suffer from disadvantages of expensive equipments, complicated synthesis processes and environment-unfriendly precursors and solvents. As a newly arisen synthesis technique, molten salt synthesis (MSS) has attracted increasing interest and been successfully used in the synthesis of a number of ceramic powders and phosphors, such as Eu^{3+} doped Y_2O_3 and Lu_2O_3 [8–11]. Very recently, Yang et al. [12] and Wu et al. [13] reported MSS of YAG:Ce^{3+} phosphor using nitrate hydrates or chloride hydrates of Y, Ce and Al as starting materials. It has been proved that the synthesis temperature can be efficiently decreased by MSS than that of the conventional solid-state reaction method. However, harmful gases including nitrogen oxides or hydrogen chloride will be released during the heating process. Therefore, it is necessary to explore new MSS methods for the synthesis of YAG:Ce^{3+} phosphors at low temperatures but avoiding using harmful precursors.

---

*Corresponding author. Tel.: +86 21 52412574; fax: +86 21 52415615.
E-mail address: ffxu@mail.sic.ac.cn (F.-F. Xu).

0272-8842/$ - see front matter
http://dx.doi.org/10.1016/j.ceramint.2013.09.051

In this work, we tried to use conventional oxides of Y, Ce and Al as raw materials in an MSS method to prepare YAG:Ce^{3+} phosphors. Influences of experimental factors including particle size of Al_2O_3 powder and heating temperature on the formation of YAG:Ce^{3+} were investigated. The formation mechanism of YAG was also discussed. It will be seen that the MSS method using oxide raw materials could be a feasible way for the synthesis of YAG:Ce^{3+} phosphors.

2. Experimental procedure

Nano-Al_2O_3 (purity 99.99%, D50 = 20 nm, γ phase) or submicron-Al_2O_3 (purity 99.99%, D50 = 0.29 μm, α phase), Y_2O_3 (purity 99.99%, D50 = 6.1 μm) and CeO_2 (purity 99.99%, D50 = 4.0 μm) were weighted according to the composition $Y_{2.94}Ce_{0.06}Al_5O_{12}$, and mixed in an agate mortar using ethanol as dispersant. After being dried, the mixed powder was combined with NaCl–KCl (mole ratio = 1:1, purity 99.99%) eutectic where the salt/oxide weight ratio was kept as 3:1. The mixture was placed in a corundum crucible with a lid and heated in a tube furnace for 3 h at various temperatures (900, 1000, 1100 and 1150 °C) under flowing N_2–H_2(5%) atmosphere. After firing, the furnace cooled down naturally to room temperature. Then the reacted mass was washed in hot de-ionized water followed by filtration for five times to remove the salts. Finally, the powders were oven-dried at 80 °C before further characterization.

Phases of the synthesized powders were identified by X-ray diffraction (XRD, AXS D8 Focus, Bruker, Germany) analysis using Cu Kα radiation ($\lambda = 1.5406$ Å) at 40 kV, 40 mA with a graphite monochromator. The step size of 0.02° was used with a scan speed of 6°/min. The powder morphology was examined by a scanning electron microscope (SEM, JSM-6390, JEOL, Japan) and a transmission electron microscope (TEM, JEM-2100F, JEOL, Japan) equipped with an energy dispersive spectrometer (EDS, INCA Energy, Oxford instruments, UK). Photoluminescence spectra were measured on a fluorescence spectrophotometer (FluoroMax-4, Horiba, Japan).

3. Results and discussion

Fig. 1 (a) shows XRD patterns of the samples using nano-Al_2O_3 as alumina source heated at different temperatures. Only hexagonal $YAlO_3$ (YAH) and YAM phases are detected in the sample synthesized at 900 °C where YAH dominates. With increasing temperature to 1000 °C and higher, YAG is formed as the dominant phase with small amounts of secondary phases of YAM and/or YAP. However, when submicron-Al_2O_3 is used as alumina source, no YAG is formed no matter of heating temperatures as can be seen in Fig. 1(b). It should be noted that either Y_2O_3 or Al_2O_3 resides in the final products with different heating temperatures, suggesting incomplete dissolution of the starting powders.

Fig. 2 (a) and (b) show SEM images of the sample synthesized at 1000 °C using nano-Al_2O_3 and submicron-Al_2O_3, respectively. The sample using nano-Al_2O_3 as alumina source consists of agglomerates of fine particles with about 1 μm in diameters. They appear in cubic or prismatic shapes, suggesting good crystallinity. Unsurprisingly, the morphology of the particles obtained using submicron Al_2O_3 is quite different and random in size and shape owing to diverse phase compositions.

The TEM image (see Fig. 3(a)) clearly shows the grain morphology of YAG agglomerates. High-resolution electron microscopy (HREM) image and electron diffraction pattern (see Fig. 3(b)) evince perfect crystallization of YAG particles. Interplanar distances of 0.49 nm and 0.30 nm correlate well with the spacing values of the (211) and (400) planes of the YAG phase, respectively. EDS spectra (see Fig. 3(c)) obtained from the framed region of Fig. 3(a) evidences that Ce ions have been incorporated into the YAG structure. Additionally, as shown in Fig. 3(d), some large agglomerates of residual nano-Al_2O_3 particles can be observed in the sample, as confirmed by the EDS analysis (see the inset of Fig. 3(d)).

Fig. 4 shows the excitation and emission spectra of the synthesized powders heated at 1000, 1100 and 1150 °C using nano-Al_2O_3 as raw material. The samples show typical emission band of YAG:Ce^{3+} in the range of 480–650 nm with the maximum intensity at 535 nm under 460 nm blue light excitation. The emission is attributed to the electron transition from the excited state of ^2D_J to the ground states of $^2F_{5/2,7/2}$ of Ce^{3+} ions doped in YAG host material [6]. Emission intensity of the sample obtained at 1100 and 1150 °C were weaker than the sample obtained at 1000 °C, probably due to the increased impurity phase content (see Fig. 1(a)).

The reaction between Y_2O_3 and Al_2O_3 was carried out after heating the reactants in NaCl–KCl eutectic for 3 h at 900 °C or higher temperatures no matter nano- or submicron-Al_2O_3 was used. All of the four phases (YAP, YAH, YAM and YAG) could be formed in such synthetic method. In MSS, two main mechanisms, "dissolution–precipitation" and "template-growth" can be involved [9,14]. In the former mechanism, all reactants must be soluble in the molten salt. The product phases are oversaturated in the melt and precipitate. In contrast, one of the reactants should be less soluble or even insoluble in the template-growth mechanism. It plays the role as a template and reacts with the more soluble reactants which dissolve in the salt and diffuse onto the surface of the template. Then it can be anticipated that different formation mechanisms will give rise to different morphologies of the products. When dissolution-precipitation mechanism dominates the reaction, the product powders do not follow the morphology of the starting powders [15]. However, in the template mechanism, the product phase retains the morphology and size of the template [14].

In the samples using nano-Al_2O_3 as starting material and heated no lower than 1000 °C, the morphology of YAG particles does not resemble that of either nano-Al_2O_3 (D50 = 20 nm) or coarse Y_2O_3 (D50 = 6.1 μm) starting powders. This suggests that dissolution-precipitation mechanism dominates the formation of YAG. MSS can provide a liquid phase environment, which can more accelerate mass transfer and diffusion than that in a solid state reaction. Thus it promotes the reaction rate and lowers the reaction temperature efficiently. According to the results of Yang et al. [12], phase pure YAG can be obtained at 400 °C in $NaNO_3$–KNO_3 melt by using nitrate hydrate raw materials or at 1000 °C in NaCl–KCl melt by using chloride

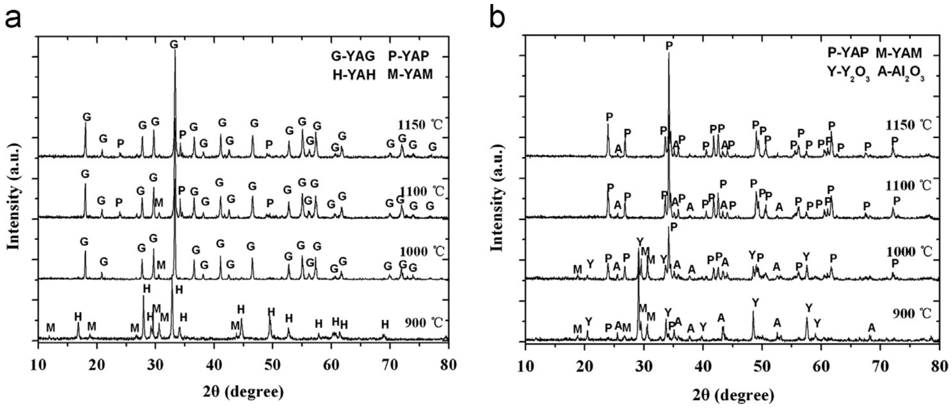

Fig. 1. XRD patterns of samples heated at different temperatures, (a) using nano-Al_2O_3, and (b) using submicron-Al_2O_3.

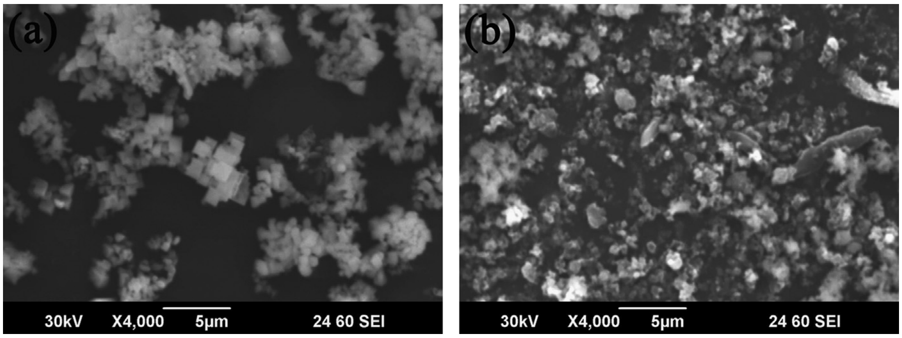

Fig. 2. SEM images of the sample synthesized at 1000 °C using (a) nano-Al_2O_3 and (b) submicron-Al_2O_3.

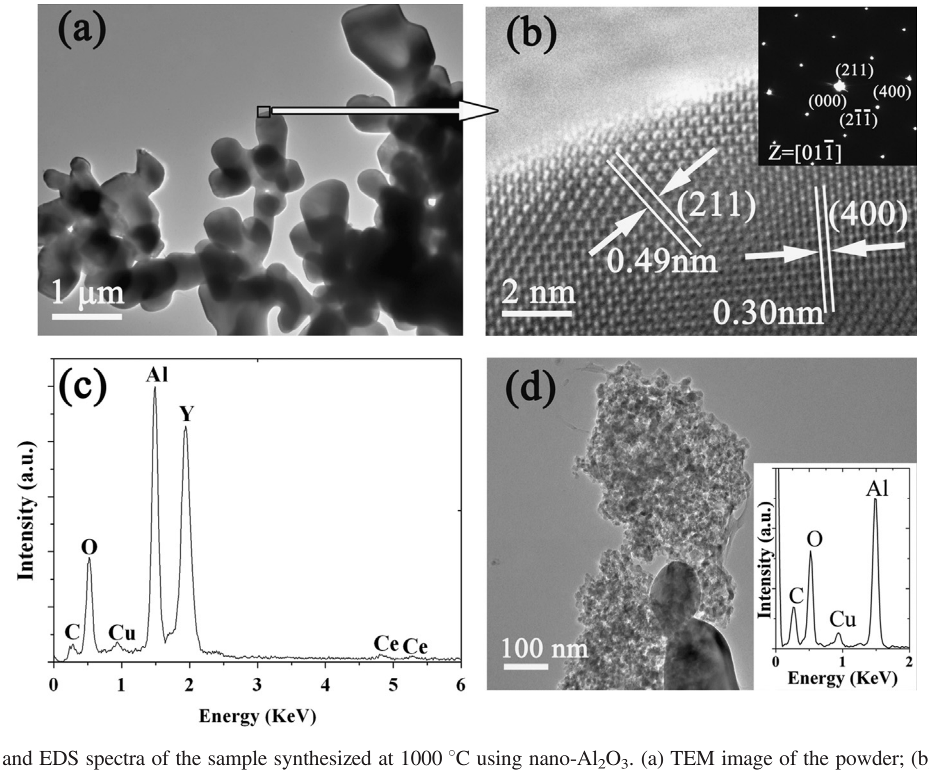

Fig. 3. TEM micrographs and EDS spectra of the sample synthesized at 1000 °C using nano-Al_2O_3. (a) TEM image of the powder; (b) [01 − 1] projected HREM image and the corresponding diffraction pattern in the inset of the framed region in (a); (c) EDS spectra of the framed region in (a); (d) TEM image of agglomerates of residual nano-Al_2O_3 particles and corresponding EDS spectra in the inset (Cu and C peaks came from copper grid and carbon-coated supporting film, respectively).

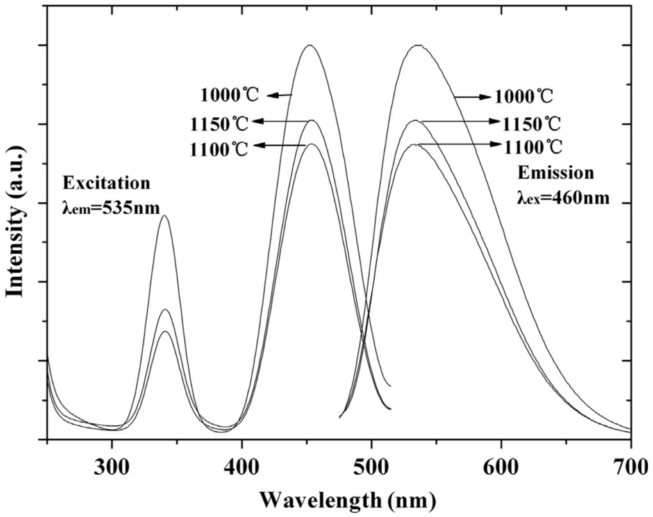

Fig. 4. Excitation (left) and emission (right) spectra of YAG:Ce^{3+} phosphors synthesized at different temperatures using nano-Al_2O_3 as raw material.

hydrate raw materials. The raw materials and molten salt media they used are mutually soluble. So the ions of Y, Ce, Al and O were mixed very homogeneously, and phase pure YAG precipitated from the melt at certain temperatures. However, in the present work, the oxide raw materials have very low solubility in the chloride melt. In the group of samples using submicron-Al_2O_3 as starting material, no YAG phase were formed at all while small amount of unreacted Al_2O_3 was detected in each sample. This implies that Al_2O_3 is less soluble or has a lower dissolution rate than Y_2O_3. Therefore, the dissolution rate is the key to the formation of YAG. Obviously, submicron-Al_2O_3 is less soluble hence less active than nano-Al_2O_3.

It is widely known that chemical reaction and phase transformation in Al_2O_3–Y_2O_3 binary system are very complicated. According to Medraj et al., in the synthesis of stoichiometric YAG, YAP and YAM by solid state reaction, the formation of these compounds started at around 1200 °C and finished by 1600 °C for YAG and by 1800 °C for both YAP and YAM [16]. Li et al. claimed that the formation of stoichiometric YAG using crystallized Al_2O_3 and Y_2O_3 prefers the conventional YAM–YAP–YAG route [17]. However, Hung et al. found that formation of YAG can be facilitated by increasing the contact points between the two oxides and using finer-sized Y_2O_3 particles. It is possible to produce pure YAG phase by a one-step thermal treatment process using submicron-sized Y_2O_3 and α-Al_2O_3, and the reaction is completed by the interface-controlled mechanism within minutes [18]. In the present work, MSS of YAG can be realized by using nano-sized Al_2O_3 particles. The morphology of the synthesized YAG grains suggests that they were formed by "dissolution–precipitation" mechanism, i.e. the reaction was finished by a one-step process. However, as mentioned before, submicron-Al_2O_3 has a lower dissolution rate than nano-Al_2O_3. When it is used as alumina source in the reaction, the concentration of dissolved Al_2O_3 in the molten salt would be too low to form YAG (Y:Al=3:5) phase, which has a higher Al content than that of YAP (Y:Al=1:1), YAH (Y:Al=1:1) and YAM (Y:Al=4:2). Therefore, Y-rich phases of YAM and/or YAP are formed, while certain amount of Al_2O_3 remains undissolved though Y_2O_3 has been completely consumed in the reaction (see Fig.1(b)). Apparently, YAM and YAP are stable with residual Al_2O_3 at various temperatures in the chloride melt and cannot transfer to YAG. When nano-Al_2O_3 is used as alumina source, full dissolution of Al_2O_3 guarantees the stoichiometry of YAG, hence the dominant formation of YAG phase. However, small amount of YAM and/or YAP particles have still been observed probably due to agglomeration of nano-Al_2O_3 particles (see Fig.3(d)), which results in uneven distribution of Al_2O_3 in the melt. According to the XRD results (see Fig.1(a)), the samples obtained at 1100 and 1150 °C seem to have more impurity phases than that of the sample heated at 1000 °C. It is possibly due to more severe agglomeration of nano-Al_2O_3 particles at higher firing temperatures. Therefore, it is possible to obtain YAG free of YAP and YAM via mixing raw powders more homogeneously to remove agglomerates of nano-Al_2O_3 particles, or along with addition of comparatively excessive nano-Al_2O_3 to the starting materials.

4. Conclusions

In summary, YAG:Ce^{3+} phosphors were prepared by molten salt synthesis method using nano-Al_2O_3, Y_2O_3 and CeO_2 as raw materials at temperatures (~1000 °C) lower than that of conventional solid-state reaction (>1600 °C). It is found that the formation of YAG is strongly dependent on the morphology of raw materials and firing temperatures. Highly active Al_2O_3 and proper reaction temperature are required to obtain YAG phase. Morphologies of the synthesized YAG:Ce^{3+} phosphor particles are completely different from that of both Al_2O_3 and Y_2O_3 raw materials, implying that "dissolution-precipitation" mechanism dominates the formation process of YAG phase. Thus, nano-Al_2O_3 starting powders promote their solution in the melt, giving a solute stoichiometric of YAG, which guarantees the formation of YAG phases. The as-prepared YAG:Ce^{3+} phosphor powders showed typical emission spectra under excitation of 460 nm blue light, indicating feasibility of molten salt synthesis method for the preparation of phosphors.

Acknowledgments

We acknowledge financial supports from the National Natural Science Foundation of China (Nos. 51272270, 60936001 and 51102265) and the National Basic Research Program of China (No. 2009CB939904).

References

[1] J.-G. Li, T. Ikegami, J.-H. Lee, T. Mori, Y. Yajima, Co-precipitation synthesis and sintering of yttrium aluminum garnet (YAG) powders: the effect of precipitant, Journal of the European Ceramic Society 20 (2000) 2395–2405.

[2] E. Zych, C. Brecher, Temperature dependence of host-associated luminescence from YAG transparent ceramic material, Journal of Luminescence 90 (2000) 89–99.

[3] T. Tamura, T. Setomoto, T. Taguchi, Illumination characteristics of lighting array using 10 cd-class white LEDs under AC 100 V operation, Journal of Luminescence 87–89 (2000) 1180–1182.

[4] H. Jiao, Q. Ma, L.-L. He, Z. Liu, Q.-L. Wu, Low temperature synthesis of YAG:Ce phosphors by LiF assisted sol–gel combustion method, Powder Technology 198 (2010) 229–232.

[5] B. Hoghooghi, L. Healey, S. Powell, J. McKitrick, E. Sluzky, L. Hesse, Synthesis of YAG:Cr phosphors by precipitation from aluminum and yttrium sulfate solutions, Materials Chemistry and Physics 38 (1994) 175–180.

[6] L. Mancic, K. Marinkovic, B.A. Marinkovic, M. Dramicanin, O. Milosevic, YAG:Ce^{3+} nanostructured particles obtained via spray pyrolysis of polymeric precursor solution, Journal of the European Ceramic Society 30 (2010) 577–582.

[7] X. Li, H. Liu, J.-Y. Wang, H.-M. Cui, F. Han, YAG:Ce nano-sized phosphor particles prepared by a solvothermal method, Materials Research Bulletin 39 (2004) 1923–1930.

[8] F. Bortolani, R.A. Dorey, Molten salt synthesis of PZT powder for direct write inks, Journal of the European Ceramic Society 30 (2010) 2073–2079.

[9] S.-W. Zhang, D.D. Jayaseelan, G. Bhattacharya, W.E. Lee, Molten salt synthesis of magnesium aluminate ($MgAl_2O_4$) spinel powder, Journal of the American Ceramic Society 89 (2006) 1724–1726.

[10] Y. Huang, Y.-S. Hu, X.-M. Teng, Z. Long, H.-Q. Ye, W.-D. Zhuang, Influence of molten salt on luminescent intensity and particle size of Y_2O_3:Eu^{3+} phosphor, Journal of Rare Earths 25 (2007) 697–700.

[11] J. Trojan-Piegza, E. Zych, Preparation of nanocrystalline Lu_2O_3:Eu phosphor via a molten salts route, Journal of Alloys and Compounds 380 (2004) 118–122.

[12] H.-J. Yang, G.-S. Zhu, L. Yuan, C. Zhang, F.-S. Li, H.-R. Xu, A.-B. Yu, Characterization and luminescence properties of YAG:Ce^{3+} phosphors by molten salt synthesis, Journal of the American Ceramic Society 95 (2012) 49–51.

[13] C.-L. Wu, A. Luo, G.-P. Du, X.-M. Qin, W.-Z. Shi, Synthesis and luminescent properties of nonaggregated YAG:Ce^{3+} phosphors via the molten salt synthesis method, Materials Science in Semiconductor Processing 16 (2013) 679–685.

[14] W.E. Lee, D.D. Jayaseelan, S.-W. Zhang, Solid-liquid interactions: The key to microstructural evolution in ceramics, Journal of the European Ceramic Society 28 (2008) 1517–1525.

[15] Z.-S. Li, S.-W. Zhang, W.E. Lee, Molten salt synthesis of $LaAlO_3$ powder at low temperatures, Journal of the European Ceramic Society 27 (2007) 3201–3205.

[16] M. Medraj, R. Hammond, M.A. Parvez, R.A.L. Drew, W.T. Thompson, High temperature neutron diffraction study of the Al_2O_3–Y_2O_3 system, Journal of the European Ceramic Society 26 (2006) 3515–3524.

[17] M.-J. Li, Y.-C. Wu, F.-S. Yen, C.-Y. Huang, Influence of ionic mobility on the phase transformation route in $Y_3Al_5O_{12}$ (YAG) stoichiometry, Journal of the European Ceramic Society 31 (2011) 2099–2106.

[18] C.-T. Hung, C.-Y. Lai, F.-S. Yen, Size ratio induced yttrium aluminum garnet formation characteristics in nano-scaled Y_2O_3–Al_2O_3 powder systems via fast firing processes, Materials Chemistry and Physics 129 (2011) 534–539.