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Synthesis of Yttrium–Aluminum–Garnet Hollow Microspheres by Reverse-Emulsion Technique

Minati Chatterjee and Milan Kanti Naskar[†]

Sol–Gel Division, Central Glass and Ceramic Research Institute, Kolkata 700 032, India

Yttrium–aluminum–garnet (YAG, $Y_3Al_5O_{12}$) hollow microspheres were synthesized by reverse-emulsion (w/o) technique starting with aqua-based precursors of oxides. The non-ionic surfactant was used as the emulsifying agent. The gel powders were calcined at 700°–1200°C. The synthesized powders were characterized by differential thermal analysis (DTA), thermogravimetry, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The appearance of an exothermic peak at 932°C in the DTA curve revealed the crystallization of YAG, which was further confirmed by XRD and FTIR studies. SEM confirmed the formation of hollow microspheres.

I. Introduction

IN recent years, there has been a keen interest in the synthesis of micro and nanometer-sized hollow spheres. The hollow powders usually exhibit some special properties that are substantially different from conventional powders, such as low density, large surface area, good surface permeability and high thermal and mechanical stability. Hollow oxide powders have been widely used for light weight and thermally insulating fillers for composites, fillers for reflective and luminescent coatings, plasma-sprayed coatings, preparation and internal confinement fusion of nuclear materials,[1] catalyst support, separation media,[2] and drug delivery agents,[3] etc. There have been a number of methods for the synthesis of hollow microspheres, such as dual nozzle reaction systems,[4] spray pyrolysis,[5] melting in DC plasma,[6] and reverse emulsion (w/o).[7]

Yttrium–aluminum–garnet (YAG, $Y_3Al_5O_{12}$) has received much attention because of its stable chemical and physical properties.[8] It is used as a host for lasers and for phosphors of high resolution.[9] Because of the neutronic inertness of its constituent atoms, porous YAG powders were used as the matrix materials for the transmutation and incineration of minor actinides in nuclear reactors.[10] It is also a promising structural materials for high-temperature engineering for insulating or refractory coatings because of its high chemical stability, low electrical conductivity, and high creep resistance.[11]

Synthesis of YAG by the conventional mixed-oxide process requires a high temperature ($\sim 1700°C$) and lengthy heat treatment to obtain phase-pure YAG. If processing temperatures are too low, the product contains intermediate phase, i.e., YAP (YAlO_3) and YAM ($Y_4Al_2O_9$).[12,13] Thus, for the synthesis of YAG at lower temperatures, several methods have been developed, in which aluminum and yttrium atoms are homogeneously mixed. The most common methods are precipitation of hydroxides,[14,15] sol–gel process,[16,17] urea method,[18] spray

pyrolysis,[19] combustion synthesis,[20] etc. However, the above methods require a temperature above 1000°C, and the prolonged heating for complete transformation into YAG causes several agglomerations in the powders exhibiting wide particle size distribution. Therefore, an intermediate milling step is adopted for obtaining the required size distribution before sintering, which of course becomes the source of impurity in the powders.

Both the microemulsion and reverse-emulsion techniques are applicable for the synthesis of micrometer and submicrometer sized particles. However, considering the advantages of hollow ceramic microspheres, in the present investigation for the preparation of agglomerate-free, micrometer-sized hollow YAG spheres, the reverse-emulsion technique has been followed using the sols of optimum viscosity ranging from 20 to 30 mPas. The novelty of the present method of preparing hollow YAG microspheres is worth mentioning in respect of low processing time, controlled particle sizes and shapes and good flowability characteristics starting with aqua-based precursor materials for the preparation of sols.[21,22]

II. Experimental Procedure

A schematic for the synthesis of hollow YAG powder is shown in Fig. 1. Calculated quantities of $Y(NO_3)_3 \cdot 6H_2O$ (Indian Rare Earth Ltd., Mumbai, India, purity >99%) and $Al(NO_3)_3 \cdot 9H_2O$ (A.R. Merck, Mumbai, India, purity >99%) with yttria–alumina mol ratio as 3:5, were dissolved in deionized water to make a bi-component solution of Y^{3+} and Al^{3+}. The pH of the bi-component solution was then adjusted up to about 3 by the addition of ammonia solution (25 wt%, G.R. Merck) under agitation. The resulting 1 M solution was heated to $80° \pm 1°C$ under controlled conditions, i.e., by slow addition of ammonia solution under vigorous stirring in a covered container. The viscosity of the sol thus obtained increased with increasing time of heating. The heating was continued until the final viscosities of the transparent, bi-component sols were determined to be 20 ± 1, 25 ± 1 and 30 ± 1 mPa·s. The pH of each sol at these stages was found to be 3.1 ± 0.02. The pH of the sols was measured with a Jencons pH meter (Model 3030, Jencons Scientific Ltd., Bedfordshire, U.K.) while the viscosity values were recorded using a Brookfied viscometer (Model LVTDV-II, Brookfield Laboratories Inc., MA).

In the present investigation, water-in-oil (w/o)-type reverse emulsions were prepared.[22] The sol prepared as above was used as the aqueous phase (w) while cyclohexane (G.R. Merck purity >99%) of dielectric constant 2.042 was used as the oil phase (o). A mixture of cyclohexane and surfactant, i.e., sorbitant monooleate (Span 80, Fluka Chemie AG, Neu-Ulm, Switzerland) with a hydrophilic/lipophilic balance (HLB) value of 4.3 acted as the support solvent. The emulsions were prepared by dispersing sols of different viscosities ranging from 20 to 30 mPa·s as droplets in the support solvent under constant agitation (150 rpm). The volume ratio of the sol:support solvent was kept constant at 1:4.

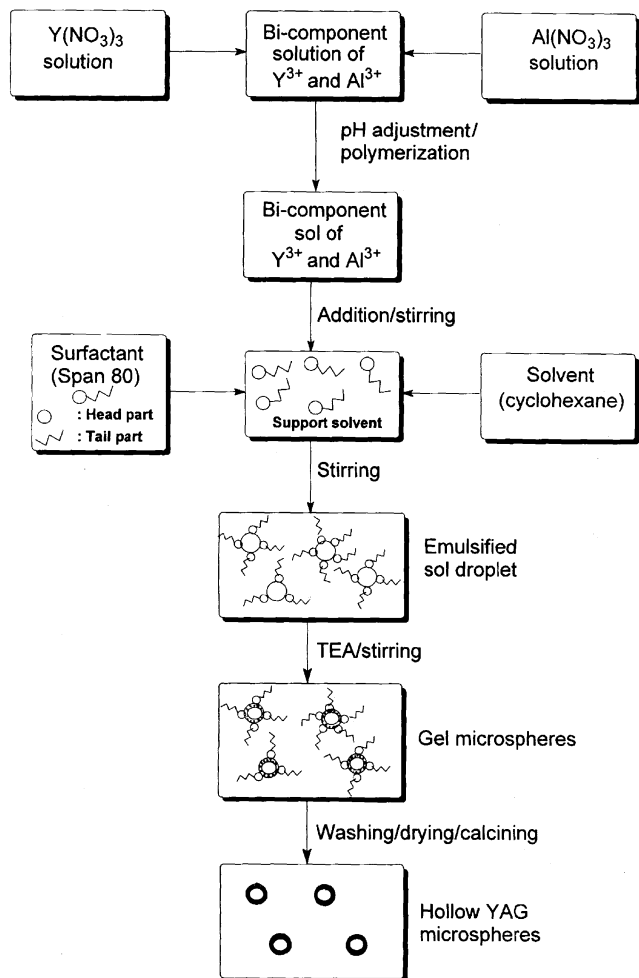---

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Fig. 1. Schematic of the preparation of yttrium–aluminum–garnet (YAG) hollow microspheres by reverse-emulsion process.

The emulsified sol droplets were converted to gel microspheres by the addition of a gelling agent, e.g., triethylamine (TEA) (G.R. Merck) under agitation until a pH of 10–12 was reached. The gel microspheres, after separating by filtration, were washed with acetone (G.R. Merck), dried at 110°C in air under static conditions and finally calcined at different temperatures in the range of 700°–1200°C, each with 1 h dwell time (in air under static conditions) to obtain the oxide microspheres.

The gel and the oxide microspheres were characterized by differential thermal analysis (DTA) and thermogravimetry (TG) (Netzsch STA 409c, M/S Netzsch Geratebau GmbH, Bayern, Germany), X-ray diffraction (XRD) (Philips PW-1730 Philips Corporation, Almelo, the Netherlands) with Ni-filtered Cu$K\alpha$ radiation, Fourier transform infrared spectroscopy (FTIR) (Nicolet 5PC, Nicolet Analytical Instruments, Madison, WI) and scanning electron microscopy (SEM) (S 430i, LEO Electronic Microscopy Ltd., Cambridge, U.K.).

III. Results and Discussion

DTA and TG curves of the gel sample are presented in Fig. 2. In the DTA curve, a sharp endothermic peak at 143°C and a broad endothermic peak at 334°C were observed. Two exothermic peaks at 231° and 932°C along with a small hump at 916°C were also revealed from the DTA curve. The sharp endothermic peak at 143°C was because of the removal of adsorbed water and other volatiles present in the sample,[22,23] while volatilization of hydroxides and structural water molecules were confirmed from the endothermic peak at 334°C.[23] The exothermic peak at 231°C indicated the decomposition of nitrates and residual organics.
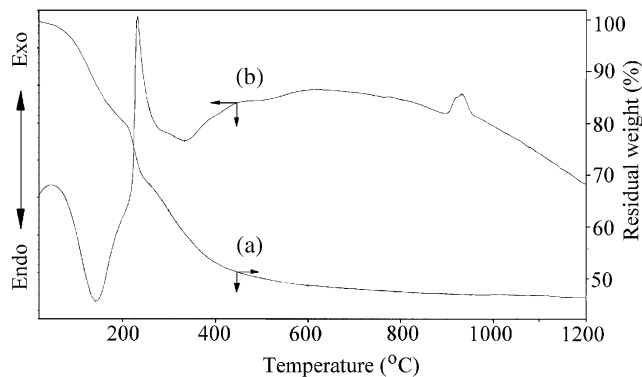

Fig. 2. Thermogravimetry (a) and differential thermal analysis (b) curves of gel microspheres of yttrium–aluminum–garnet composition.

The small exothermic peak at 916°C was because of the crystallization of YAM ($Y_4Al_{12}O_9$), and the broad exothermic peak at 932°C was attributed to the crystallization of YAG.[24] The above results were further confirmed by XRD.

From the TG curve of the same sample, a maximum weight loss of about 52%, corresponding to the removal of water molecules and other decomposable materials, was noticed up to a temperature of about 600°C followed by a negligible amount of weight loss (about 2%) up to 1200°C.

To study the crystallization behavior of the YAG gel powders calcined at 700°–1200°C, XRD patterns were recorded (Fig. 3). They show that the powder remained almost amorphous up to 800°C. A crystallization of YAM, $Y_4Al_{12}O_9$ (JCPDS No. 34–368)
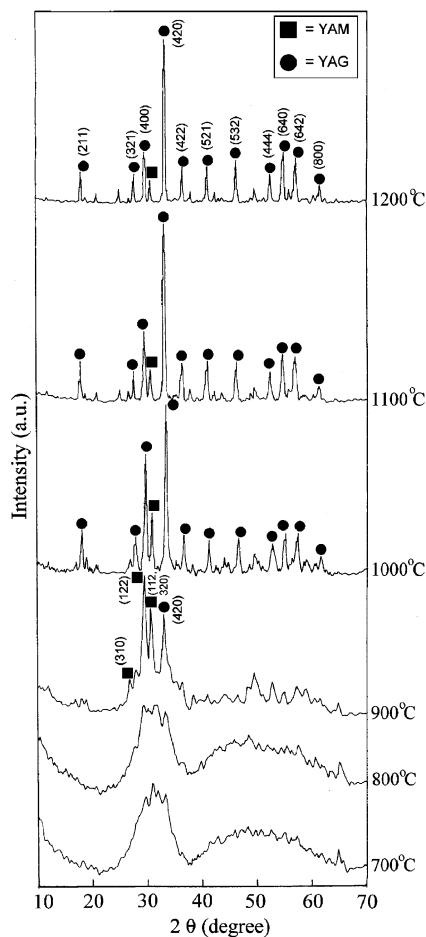

Fig. 3. X-ray diffraction patterns of microspheres of yttrium–aluminum–garnet composition calcined at different temperatures: (a) 700°C, (b) 800°C, (c) 900°C, (d) 1000°C, (e) 1100°C, and (f) 1200°C with a dwell time of 1 h in each case.

Fig. 4. Fourier transform infrared spectroscopy spectra of microspheres of yttrium–aluminum–garnet composition calcined at different temperatures: (a) 700°C, (b) 800°C, (c) 900°C, (d) 1000°C, (e) 1100°C, and (f) 1200°C with a dwell time of 1 h in each case.
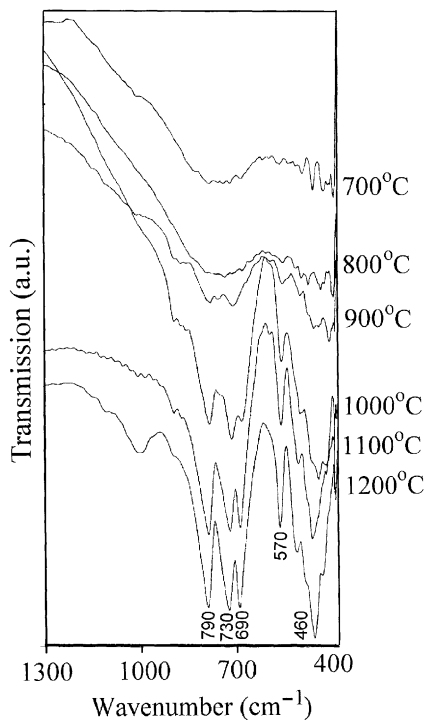
along with a small amount of YAG, $Y_3Al_5O_{12}$ (JCPDS No. 33–40) appeared at 900°C. Almost complete crystallization of cubic YAG occurred at 1000°C, and it retained up to 1200°C. From Fig. 3, it is obvious that the intensity of YAG peaks increased with increase in temperature from 1000° to 1200°C. However, some very small unidentified peaks are observed with YAG and YAM at 1000°–1200°C.

To examine the characteristics of the products calcined at different temperatures, FTIR spectra of the powders calcined at 700°–1200°C were recorded in the wavenumber range 4000–400 cm^{-1}; however, the spectra in the wavenumber region 1300–400 cm^{-1} are presented in Fig. 4. The strong absorption bands at 460, 570, 690, 730, and 790 cm^{-1} observed at 1000°–1200°C were the characteristic bands for YAG.[8,25] It is to be noted that the above bands were absent at 700°–800°C but a weak appearance of the same at 900°C indicated the initiation of YAG crystallization, which was also confirmed by XRD.

Figures 5(a)–(c) show the SEM micrographs of oxide powders with the average particle sizes 20, 30, and 50 μm obtained from the sols of viscosities 20, 25, and 30 mPa·s, respectively, followed by their calcination at 1200°C/1 h each. It was clear that with an increase in viscosity of the sol, particle size became larger and broken. Hollow microspheres with the spherical cavities could be identified from the fractured particles (Fig. 5).

The mechanism of formation of hollow microspheres by reverse emulsion has already been discussed in our earlier work.[7] The effects of the type of solvents, surfactants, and their molar compositions played an important role in controlling particle sizes and shapes. However, the role of viscosity of the aqueous sol is also noteworthy for controlling the same. In the present case, for the microspheres obtained from the sol of relatively low viscosity (20 mPa·s), the shell formation with less dense network and high permeability to both TEA and cyclohexane occurred toward the interior part of the droplet, making the shell formation process complete. Repeated washings of these microspheres with acetone under vacuum helped the trapped liquid to come out gradually through the highly permeable shell. Final removal of acetone under vacuum formed gel microspheres, with the internal cavity free from any trapped liquid. Under such
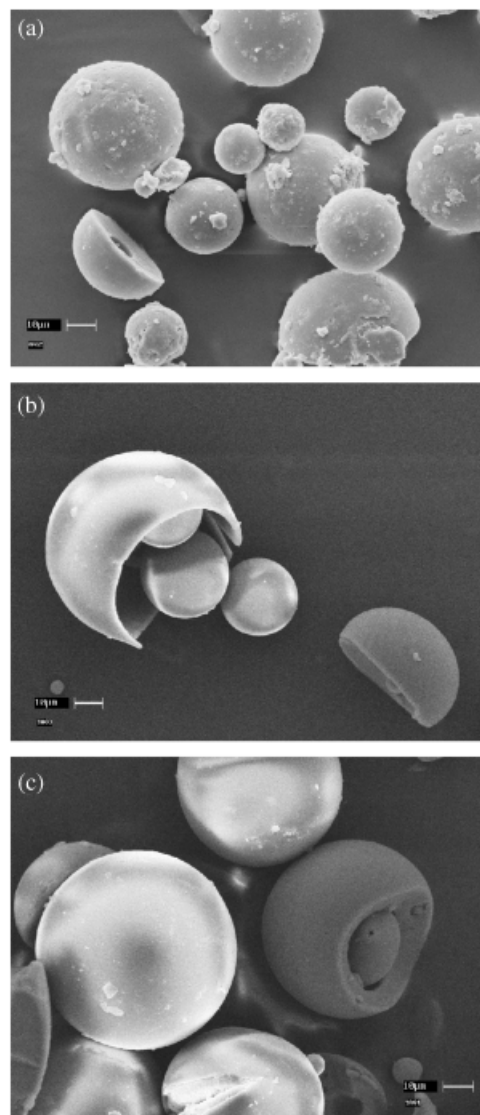

Fig. 5. Scanning electron microscopy micrographs of yttrium–aluminum–garnet hollow microspheres obtained from the sols of viscosities (a) 20 mPa·s; (b) 25 mPa·s, and (c) 30 mPa·s.

a condition, formation of mostly unbroken and hollow YAG microspheres were obtained after calcination.

In case of microspheres obtained from a sol of relatively high viscosity (30 mPa·s), gel formation occurred, giving rise to a dense and low permeable shell. During calcination of these washed microspheres, the removal of the volatiles from the entrapped liquid was believed to be hindered. This caused a generation of internal pressure with the formation of fractured microspheres. Under such conditions, the spheres obtained from relatively high viscosity of the sol became larger and mostly broken.

IV. Conclusions

YAG hollow microspheres were synthesized by reverse-emulsion (w/o) method. The exothermic peak at 932°C in the DTA curve showed the crystallization of YAG, which was further confirmed by XRD results. Almost complete crystallization of cubic YAG, $Y_3Al_5O_{12}$ occurred at 1000°C. The strong absorption bands at 460, 570, 690, 730 and 790 cm^{-1} observed at 1000°–1200°C from FTIR were the characteristic bands for YAG. SEM micrographs showed the hollow microspheres of YAG with the average particle sizes 20, 30 and 50 μm obtained from the sols of viscosities 20, 25, and 30 mPa·s, respectively. The spheres obtained from high viscosity of the sol became larger and mostly broken.

References

[1] J. G. Liu and D. L. Wilcox Sr., "Factors Influencing the Formation of Hollow Ceramic Microspheres by Water Extraction of Colloid Droplets," *J. Mater. Res.*, **10** [1] 84–95 (1995).

[2] D. Walsh, B. Lebeau, and S. Mann, "Morphosynthesis of Cacium Carbonate (Vaterite) Microsponges," *Adv. Mater.*, **11** [4] 324–8 (1999).

[3] F. Caruso, R. A. Caruso, and H. Mohwald, "Nanoengineering of Inorganic and Hybrid Hollow Spheres by Colloid Templating," *Science*, **282** [5391] 1111–4 (1998).

[4] K. K. Kim, K. Y. Jang, and R. S. Upadhye, "Hollow Silica Spheres of Controlled Size and Porosity by Sol–Gel Processing," *J. Am. Ceram. Soc.*, **74** [8] 1987–92 (1991).

[5] A. M. Gadalla and H.-F. Yu, "Preparation of Fine Hollow, Spherical $NiFe_2O_4$ Powders," *J. Mater. Res.*, **5** [12] 2923–7 (1990).

[6] G. Pravdic and M. S. J. Gani, "The Formation of Hollow Spherical Ceramic Oxide Particles in a d.c. Plasma," *J. Mater. Sci.*, **31** [13] 3487–95 (1996).

[7] M. K. Naskar, M. Chatterjee, and N. S. Lakshmi, "Sol–Emulsion–Gel Synthesis of Hollow Mullite Microspheres," *J. Mater. Sci.*, **37**, 343–8 (2002).

[8] X. Li, H. Liu, J. Wang, H. Cui, and F. Han, "Production of Nanosized YAG Powders with Spherical Morphology and Nonaggregation Via Solvothermal Method," *J. Am. Ceram. Soc.*, **87** [12] 2288–90 (2004).

[9] K. M. Kinsman and J. Mckittrick, "Phase Development and Luminescence in Chromium-Doped Yttrium Aluminum Garnet (YAG:Cr) Phosphor," *J. Am. Ceram. Soc.*, **77** [11] 2866–72 (1994).

[10] A. Fernandez and J. Somers, "Highly Porous Yttrium Aluminium Garnet (YAG) Particles Synthesized by a Gel Supported Precipitation (GSP) Process," *J. Mater. Sci.*, **38** [11] 2331–5 (2003).

[11] G. S. Corman, "High-Temperature Creep of Some Single Crystal Oxides," *Ceram. Eng. Sci. Proc.*, **12** [9–10] 1745–66 (1991).

[12] I. Warshaw and R. Roy, "Stable and Metastable Equilibria in the Systems Y_2O_3–Al_2O_3 and Gd_2O_3–Fe_2O_3," *J. Am. Ceram. Soc.*, **42** [9] 434–8 (1959).

[13] J. S. Abell, I. R. Harris, B. Cockayne, and B. Lent, "An Investigation of Phase Stability in the Y_2O_3–Al_2O_3 Systems," *J. Mater. Sci.*, **9** [4] 527–37 (1974).

[14] P. Apte, H. Burke, and H. Pickup, "Synthesis of Yttrium Aluminum Garnet by Reverse Strike Precipitation," *J. Mater. Res.*, **7** [3] 706–11 (1992).

[15] J.-G. Li, T. Ikegami, J.-H. Lee, and T. Mori, "Low-Temperature Fabrication of Transparent Yttrium Aluminum Garnet (YAG) Ceramics Without Additives," *J. Am. Ceram. Soc.*, **83** [4] 961–3 (2000).

[16] T. Tachiwaki, M. Yoshinaka, K. Hirota, T. Ikegami, and O. Yamaguchi, "Novel Synthesis of $Y_3Al_5O_{12}$ (YAG) Leading to Transparent Ceramics," *Solid State Commun.*, **119** [10–114] 603–6 (2001).

[17] G. Gowda, "Synthesis of Yttrium Aluminates by the Sol–Gel Process," *J. Mater. Sci. Lett.*, **5** [10] 1029–32 (1986).

[18] N. Matsashita, N. Tsuchiya, K. Nakatsuka, and T. Yanagitani, "Precipitation and Calcinations Processes for Yttrium Aluminum Garnet Precursors Synthesized by the Urea Method," *J. Am. Ceram. Soc.*, **82** [8] 1977–84 (1999).

[19] M. Nymen, J. Caruso, M. J. Hampden-Smith, and T. T. Kodas, "Comparison of Solid-State and Spray-Pyrolysis Synthesis of Yttrium Aluminate Powders," *J. Am. Ceram. Soc.*, **80** [5] 1231–8 (1997).

[20] S. Roy, L. Wang, W. Sigmund, and F. Aldingir, "Synthesis of YAG Phase by a Citrate–Nitrate Combustion Technique," *Mater. Lett.*, **39** [3] 138–41 (1999).

[21] M. Chatterjee, M. K. Naskar, B. Siladitya, and D. Ganguli, "Role of Organic Solvents and Surface-Active Agents in the Sol–Emulsion–Gel Synthesis of Spherical Alumina Powders," *J. Mater. Res.*, **15** [1] 176–85 (2000).

[22] M. K. Naskar and M. Chatterjee, "Magnesium Aluminate ($MgAl_2O_4$) Spinel Powders from Water-Based Sols," *J. Am. Ceram. Soc.*, **88** [1] 38–44 (2005).

[23] J.-G. Li, T. Ikegami, J.-H. Lee, T. Mori, and Y. Yajima, "Co-Precipitation Synthesis and Sintering of Yttrium Aluminum Garnet (YAG) Powders: The Effect of Precipitant," *J. Eur. Ceram. Soc.*, **20** [14–15] 2395–405 (2000).

[24] X. Guo, P. S. Devi, B. G. Ravi, J. B. Parise, S. Sampath, and J. C. Hanson, "Phase Evolution of Yttrium Aluminum Garnet (YAG) in a Citrate–Nitrate Gel Combustion," *J. Mater. Chem.*, **14**, 1288–92 (2004).

[25] L. M. Seaverson, S.-Q. Luo, P.-L. Chien, and J. F. McClelland, "Carbonate Associated with Hydroxide Sol–Gel Processing of Yttria: An Infrared Spectroscopic Study," *J. Am. Ceram. Soc.*, **69** [5] 423–9 (1986). □