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The sonochemical and microwave-assisted synthesis of nanosized YAG particles

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Nanoparticles of YAG were prepared by sonochemistry and by microwave radiation. In both cases, the last stage of the preparation was annealing at a high temperature, which led to a highly aggregated product. To reduce the aggregation we have added κ-carrageenan (a sugar) to the reaction mixture. The effect of the sugar is presented and discussed herein.

Introduction

Ceramics based on the Y_2O_3–Al_2O_3 formula are promising materials for optical, electronic and structural applications. The composition of $3Y_2O_3$:$5Al_2O_3$, commonly called yttrium aluminium garnet (YAG, $Y_3Al_5O_{12}$), exists in a cubic form with a garnet structure. When YAG is doped with a transition metal or a lanthanide element it becomes an important solid-state laser material, widely used in luminescence systems, as well as a window material for a variety of lamps. In view of its high thermal stability[1] and an extremely high creep resistance, YAG is a promising fiber material for the preparation of ceramic composites. The electrical conductivity of YAG is also reported to be lower than that of any other polycrystalline oxide. Owing to there being such wide and diverse potential applications for YAG-based ceramics, new routes for the synthesis of pure and homogeneously-doped yttrium aluminium garnet are highly desired.[2,3]

There are three stable phases of the Y_2O_3–Al_2O_3 system. The first has the composition $Y_4Al_2O_9$ (YAM- monoclinic), the second $YAlO_3$ (YAP-orthorhombic or hexagonal structure) and the third $Y_3Al_5O_{12}$ (YAG).[1,4–6] In all of the various synthetic methods for the synthesis of YAG nanoparticles (nanoYAG), the prepared product is amorphous. The crystallization process to form a YAG phase starts at 800 °C, and it completely transforms into YAG below 900 °C. A certain amount of the YAM phase co-exists with the YAG phase between 850 °C and 900 °C, but above 900 °C, only the YAG phase exists.[4]

The final product of calcination and its behavior is greatly influenced by the nature of the starting precursor powder. Thus, it is important to understand the conversion mechanism of precursor into crystalline YAG in order to control the nature of the final product.[1]

The solid-state synthesis of YAG ceramic from Al_2O_3 and Y_2O_3 powders usually requires extensive mechanical mixing and lengthy heat treatments above 1600 °C.[4] These processing conditions do not allow facile control over micro-structure, grain size and grain size distribution in the resulting powders or shapes. Several wet chemical techniques were reported for the synthesis of YAG, and methods such as the polymerized complex route,[7] metal–organic preceramic processing,[8] coprecipitation methods[9,10] and the yttrium carboxylate–alumoxane route[11] have been used to produce YAG phases. Most of these methods suffer from being complex as well as time consuming (long refluxing times, gelation periods of several days, *etc.*) and/or there being mismatches in the solution behaviour of the constituents.[2]

With the growing interest in nanotechnology, special synthetic routes have been developed for the preparation of nanoYAG particles. The nanoparticles were prepared by sol–gel methods,[2] a citrate–nitrate gel combustion process[1–3] and a precipitation method.[12]

In this paper we report on the application of ultrasound and microwave radiation to the synthesis of nanoYAG particles. Nanosized particles were obtained by a sonochemical reaction, as well as by microwave dielectric heating. The products of the sonochemical reaction varied in size, shape, structure and in their solid phase (amorphous or crystalline), but they were always of nanometre size.[13] The microwave reaction was conducted in a regular domestic microwave oven and did not require special hydrothermal equipment. In most experiments the microwave reaction was complete within a few minutes, and within 1 h at the most.[14,15]

Experimental

All the reagents were of the highest commercially-available purity. Yttrium oxide, aluminium nitrate nonahydrate and κ-carrageenan were purchased from Aldrich and used without further purification. The X-ray diffraction patterns of the products were recorded with a Bruker AXS D8 Advance Powder X-ray Diffractometer (using Cu-Kα l ∼ 1.5418 Å radiation). Peak fitting and lattice parameter refinement were computed using the Topas and Metric programs (Bruker Analytical X-Ray Systems). The morphologies and micro- or nanostructures of the synthesized products were further characterized with a JSM-840 SEM. EDAX measurements were performed on an X-ray microanalyzer (Oxford Scientific) built on a JEOL JSM-840 SEM. High resolution SEM (HR-SEM) micrographs were obtained using a Field Emission Hitachi S-2300. The transmission electron micrographs (TEM) were

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imaged on a JEOL-JEM 100SX microscope using a 100 kV accelerating voltage. Samples for TEM were prepared by placing a drop of the sample suspension on a copper grid (400 mesh, Electron Microscopy Sciences) coated with carbon film. The grid was then air dried. High resolution TEM (HRTEM) micrographs were taken using a JEOL 3010 with a 300 kV accelerating voltage. A conventional monochrome CCD camera with a resolution of 768 × 512 pixels was used to digitize the images. The digital images were processed with the Digital Micrograph software package (Gatan, Inc., Pleasanton, CA, USA). FTIR spectra were recorded in KBr pellets using an Impact 410 Nicolet spectrometer. DSC was carried out on a Mettler Toledo TC 15 using nitrogen or argon as a purging gas at a scanning rate of 5 °C min^{-1}. TGA was performed on a Mettler Toledo TGA/SDTA851 instrument using nitrogen or argon as a purging gas, also at a scanning rate of 5 °C min^{-1}.

Specific surface areas were measured by the BET method at 77 K using N_2 gas as an absorbent, after heating the sample at 120 °C for 1 h.

The C, H, N and S analyzer was made by the Thermo Electron Corporation (Model Flash EA, 1112).

Ultrasonic irradiation was provided with a high intensity ultrasonic probe (Misonix XL Sonifier, 1.13 cm diameter Ti horn, 20 kHz, 60 W cm^{-2} measured calorimerically at 60% efficiency) immersed directly into the reaction solution. The microwave-assisted reaction was carried out in a Spectra 900 W microwave oven, with a 2.45 GHz working frequency. The oven was modified to include a refluxing system. In all the experiments the microwave oven was cycled as follows: on for 21 s, off for 9 s, with the total power always at 900 W. This cycling mode was chosen in order to reduce the risk of superheating the solvent. All reactions were conducted under air.

Synthesis

Procedure for sonochemical reaction. The two reactants, $Al(NO_3)_3 \cdot 9H_2O$ and $Y(NO_3)_3$, were mixed to form the starting aqueous solution. $Y(NO_3)_3$ was prepared by dissolving 0.847 g of Y_2O_3 (0.0075 mol yttrium) in a small amount of a concentrated HNO_3 solution. After the dissolution of the oxide, the solution was evaporated, leaving only the solid nitrate. This solid was introduced into the mixed solution of the Al and Y nitrates. A typical precursor solution was prepared by mixing 4.68 g of $Al(NO_3)_3 \cdot 9H_2O$ (0.0125 mol) and 0.847 g of $Y(NO_3)_3$ (0.0075 mol) in 200 cm^{-3} of water. Thus, the molar ratio of $Al^{+3} : Y^{+3} = 0.0625 : 0.0375 = 1.67 : 1$. An aqueous ammonia solution was added to the sonication cell prior to the irradiation, keeping the pH in the 7–8 range. The solution was sonicated for 1 h without cooling the irradiated solution. The temperature at the end of the sonication reached 80 °C. The precipitate was separated from the solution by centrifugation and was washed with ethanol and water three times. The product was dried under vacuum at rt. The heating rate for the conversion of the prepared material into the crystalline phase was 10 °C min^{-1}.

Sonication in the presence of κ-carrageenan (a sugar). The highly aggregated form of the nanoYAG obtained in our experiments led to an attempt to de-aggregate the annealed product. For this purpose we added 0.22 g of κ-carrageenan to the above-mentioned sonicated mixture of $Al(NO_3)_3$ and $Y(NO_3)_3$. The sugar was added prior to the addition of ammonia. After its addition, the solution was heated to 50 °C for about 1 h to allow its dissolution, and only then was the ammonia added, keeping the pH between 7 and 8. The sonication time and conditions were identical to the experiments without κ-carrageenan. Since the κ-carrageenan is sensitive to light, the sonication cell was wrapped in aluminium foil.

The microwave (MW) synthesis of nanoYAG. The composition of the irradiated solution was identical to that of the sonochemical solution, except that NaOH replaced ammonia in creating the basic conditions. The sample was irradiated under ambient conditions for 10 min. The temperature at the end of the reaction was not measured. However, it is assumed that it was about 10 °C above the boiling point due to the superheating phenomenon.

Results and discussion

The colour of the prepared and annealed materials was white. The annealed sample underwent a series of standard characterization measurements to determine its composition and morphology. The results will be presented for both the sonochemical and MW products.

Powder XRD studies

The X-ray diffraction patterns of the samples annealed at different temperatures are shown in Fig. 1. These samples resulted from the sonochemical reaction. Fig. 1 exhibits the results of calcination for 1 h at 800 °C and 900 °C. Fig. 1a shows that the ash annealed at 800 °C is amorphous, while the sample calcined at 900 °C has a crystalline YAG phase (Fig. 1b). The sizes of the nanocrystals (at 900 °C) were calculated by using the Debye–Scherrer (DS) equation[14] and were found to be in the range 17–20 nm.

As explained above, for the MW reaction, two bases for establishing the pH of 7–8 have been examined, *i.e.*, ammonia and NaOH. The results of the powder XRD analysis for the MW annealed samples are shown in Fig. 2. The basic conditions were formed by the use of NaOH. Fig. 2 shows only the diffraction patterns for the sample annealed at 900 °C. The reason why the 1000 °C XRD pattern is not presented is because that, at this temperature, it is identical to that depicted in Fig. 1b; in other words, only the YAG phase is detected. EDAX measurements showed that there are no sodium atoms in the final product. On the other hand, the sample annealed at 900 °C reveals two phases, YAG and YAP. Raising the calcination temperature to 1000 °C (and annealing for 1 h) resulted in a pure phase of YAG. The sizes of the 1000 °C calcined nanocrystals were calculated to be in the range 19 ± 2 nm. Thus, the comparison between the sonochemical and the MW product, based on the XRD results, shows that sonication is advantageous, already yielding the YAG phase at 900 °C, while at that temperature, YAG and YAP phases are observed for the MW product. Since the calculated particle sizes are almost equal for the two products, we will attribute the difference between them to the MW method yielding more defects and pores than the sonochemical technique. Thus, in the conversion to the stable YAG phase, a higher temperature is required.

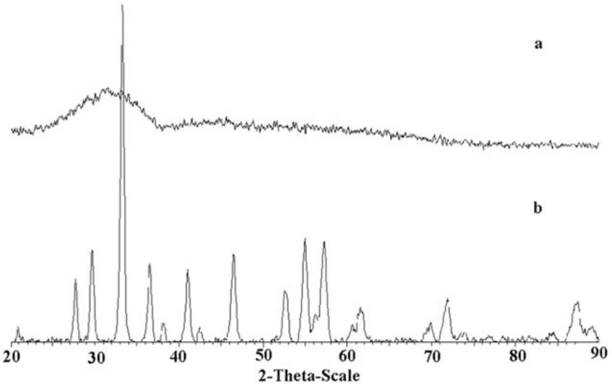

Fig. 1 The XRD patterns of the sonochemically-prepared powder calcined at (a) 800 °C and (b) 900 °C, for 1 h.

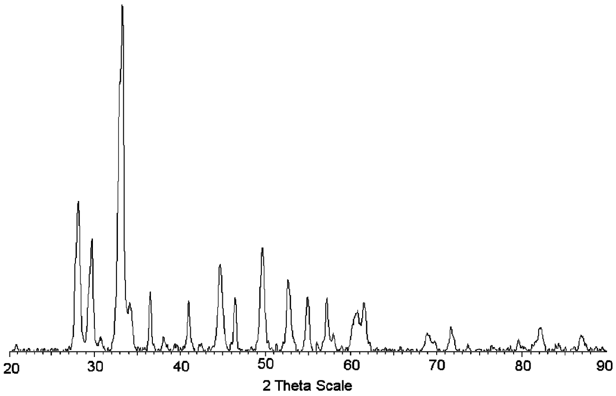

Fig. 2 The XRD patterns of the MW-prepared nanoYAG calcined at 900 °C. The basic conditions were established by the use of NaOH.

The MW reaction was also conducted using ammonia for determining the pH. The XRD patterns of the product annealed at 900 °C (Fig. 3) indicate that an amorphous material is obtained. The failure to obtain a YAG phase led us to replace the ammonia with NaOH. We can interpret these results in the following way: it is possible that ammonia easily evaporates upon MW irradiation and therefore the pH varies accordingly. Another possible explanation attributes this behavior to NaOH being a stronger electrolyte and better at absorbing the MW radiation. Thus, the amorphous product obtained is composed of smaller particles and its crystallization to the stable phase can be carried out at lower temperatures. Ammonia, on the other hand, is a weaker electrolyte that does not absorb the radiation as well, and thus fewer hot spots are formed in the liquid and a lower temperature develops. The crystallization temperature will therefore be higher than with NaOH.

In addition to the sonochemical and MW reactions, two control experiments were also conducted. In the first, a room temperature reaction was undertaken using the same concentrations of reactants as in the sonochemical and MW reactions, but without applying ultrasound or MW radiation. The second control experiment was carried out sonochemically and with MW at 100 °C. The two reactions were performed for 1 h. In both cases the annealed sample contained an impurity phase. Diffraction peaks at $2\theta = 25.25$, 26.8 and 44.8° were detected.

FTIR studies of the sonochemical reaction

Fig. 4a shows the FTIR spectrum of the sonochemically-prepared product. The spectrum illustrates a broad absorption band around 3500 cm^{-1}, which is assigned to the O–H stretching vibration of the water. The peaks in the 1100–1700 cm^{-1} region can be assigned to the vibrations of the nitrate group. Fig. 4b depicts the spectrum of the heat-treated sample. It shows only metal–oxygen vibrations which, in accordance with earlier reports, are characteristic of Y–O and Al–O stretching frequencies.[2] The 3500 cm^{-1} and 1100–1700 cm^{-1} vibrational peaks have disappeared due to the removal of water and nitrate moieties. In short, the comparison of the current FTIR spectra with those obtained by other techniques shows that the sonochemically-obtained product has an identical IR spectrum to the previous data.

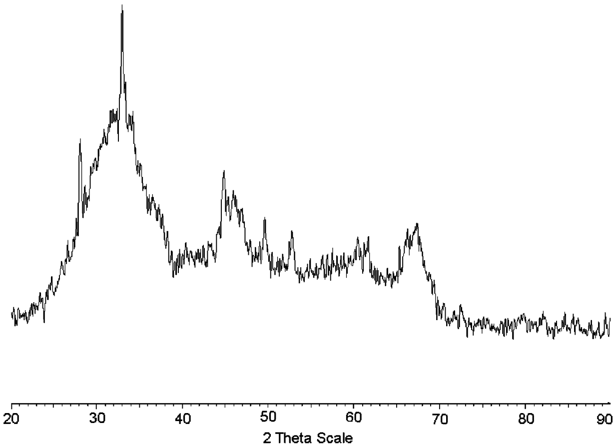

Fig. 3 The XRD patterns of the MW-prepared powder assisted by the use of ammonia and calcined at 900 °C.

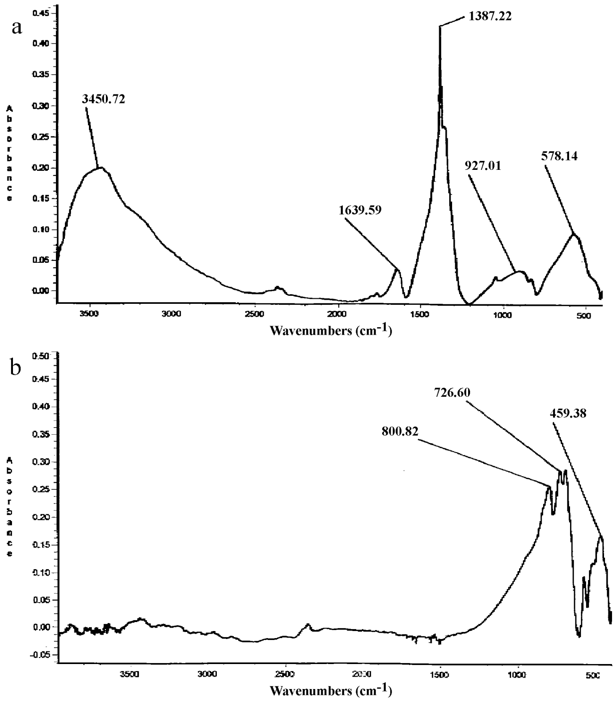

Fig. 4 FTIR spectrum of the sonochemically-prepared nanoYAG, (a) the prepared material, (b) sample after sintering.

To learn more about the content and purity of the prepared material, TGA measurements were carried out. The TGA data indicated that a weight loss of 39% happens between room temperature and 900 °C. The major part of the weight loss occurs in the temperature range of 100–500 °C; this mass loss being due to the evolution of the water, NO and NO_2. The latter gases are evolved due to the decomposition of nitrate ions present in the ash.[4]

TEM and HRTEM results of the sonochemical reaction

The TEM image of the sonochemical nanoYAG sample heated at 900 °C is illustrated in Fig. 5. The picture shows an aggregated network of small nanocrystals. The size of the nanocrystallites varies from 20–25 nm and is in good agreement with the XRD results.

A comparison between the two pictures (Fig. 5 and Fig. 6) reveals that, in both cases, almost identically-sized particles form a network of aggregated particles. The nanometric character of the products is clear in both syntheses, but the necessity to anneal the product leads to the formation of agglomerates.

The HRTEM micrograph of sonochemically-synthesized nanoYAG crystals is depicted in Fig. 7. The HRTEM lattice micrograph shows nanoYAG particles which have different crystallographic orientations. The lattice fringes are distinct and the distance between adjacent fringes in the particle's core is 0.384 nm, which correlates well with the (321) planes of the body-centered cubic YAG phase.

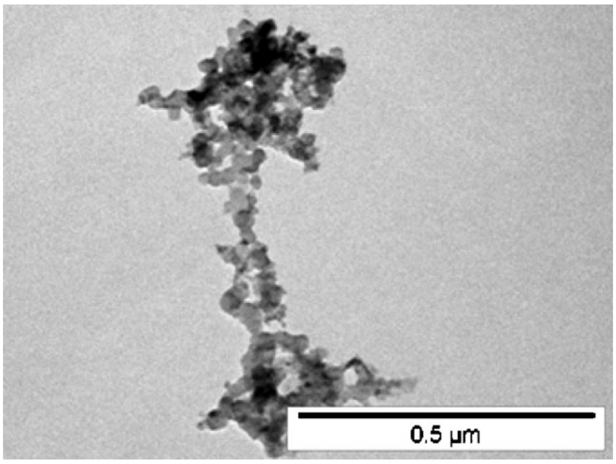

Fig. 5 TEM image of the nanoYAG product of the sonochemical process after annealing at 900 °C.

SEM measurements of the sonochemical products

The SEM micrographs of the nanoYAG crystals obtained sonochemically and calcined at 900 °C are shown in Fig. 8. Fig. 8a shows the high degree of aggregation that the nanoYAG crystallites undergo upon calcination. Fig. 8b however, shows that the addition of κ-carrageenan helps in breaking up the agglomerates. The reason for the use of κ-carrageenan is to separate the Al^{3+} ions from the Y^{3+} ions already in the solution, so that when the sugar is adsorbed into the nanoYAG particles, it prevents their aggregation. The sugar is subsequently burnt off from the nanoYAG during the calcination process. A C, H, N and S analysis of the annealed product revealed 0.023% of carbon and 0.065% of hydrogen. These results show that the sugar is completely removed in the heating process. The particle sizes measured for the products obtained after the calcination of the sugar-added product are 22 ± 3 nm.

To learn more about the nature of the products, and to show the difference in the aggregation of the nanoYAG and the nanoYAG resulting from the sugar treatment, high magnification SEM measurements were performed. Both of the micrographs in Fig. 9 show that the particles were sintered by the calcination process. It is also seen from both pictures that rounded particles (close to spherical) are glued to each other. The size of the nanoYAG particles in Fig. 9a is 1 μm, while the size of the sugar-treated nanoYAG particles in Fig. 9b is 50 nm. Since the TEM and the XRD results yielded only a 25 nm particle size, we propose that the SEM is observing an agglomerate of two particles. This shows that the annealing process and the partial sintering of the particles are not completed, and a nanometric nature is maintained by the sugar-treated particles.

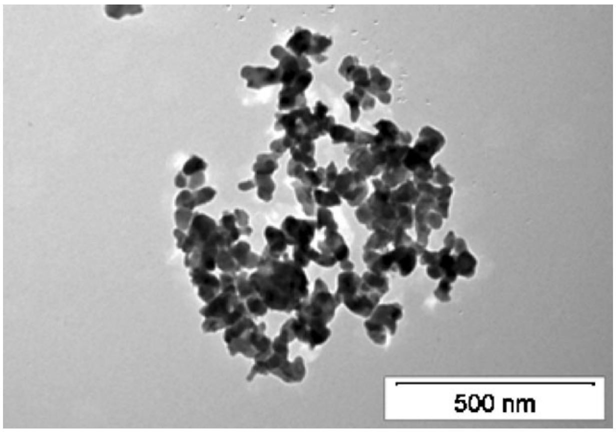

Fig. 6 TEM image of the nanoYAG product obtained by a MW process annealed at 1000 °C.

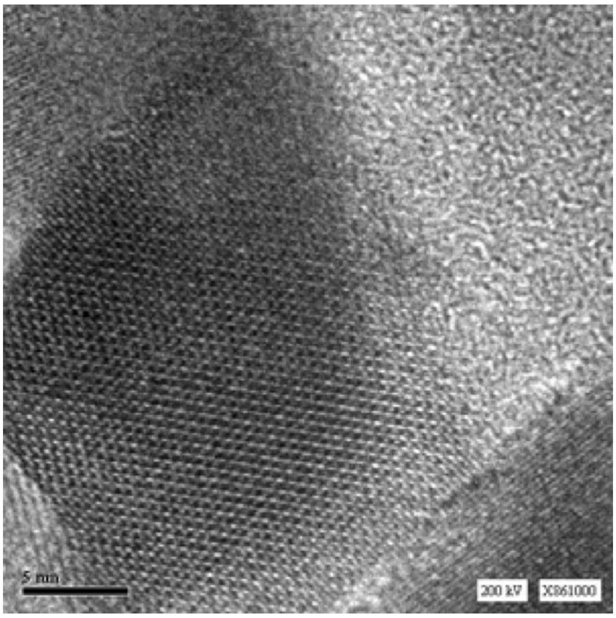

Fig. 7 HRTEM image of nanoYAG. The scale of the bar is 5 nm.

BET measurements

The nanosize nature of the products obtained by MW and sonochemical syntheses was also examined by surface area measurements. There is a big difference in the measured surface area of products obtained by the two procedures. The BET

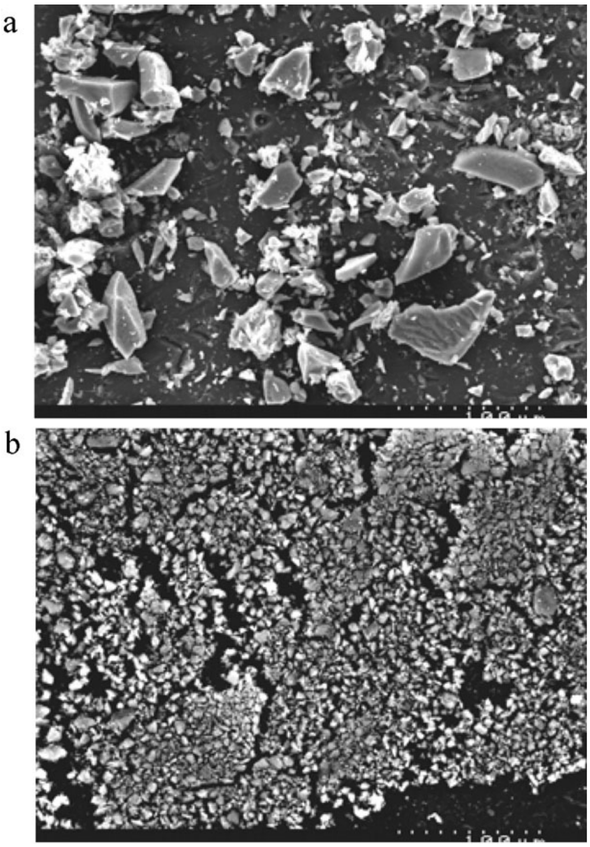

Fig. 8 SEM images of (a) nanoYAG and (b) nanoYAG + κ-carrageenan. Scale bars = 100 μm. Samples calcined at 900 °C.

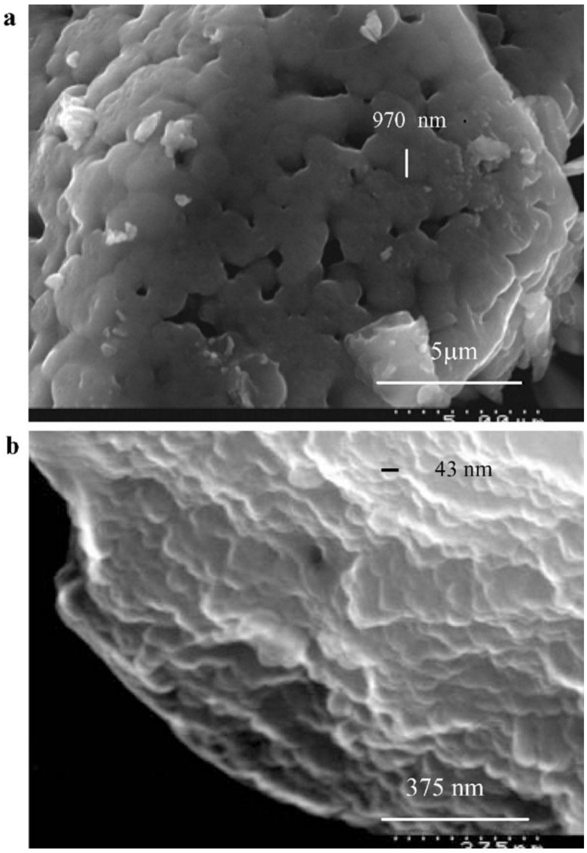

Fig. 9 SEM images of (a) nanoYAG (sonochemical), scale bar = 5 µm and (b) nanoYAG (sonochemical) treated with κ-carrageenan, scale bar = 375 nm. Both samples were calcined at 900 °C.

surface area of the microwave product after calcination at 1000 °C was 24 ± 2 m^2g^{-1}. When the microwave reaction time was increased from 10 min to 30 min, an increase in the surface area to 42 ± 4 m^2g^{-1} was measured. It should be noted that the particle size for the annealed products of the 10 and 30 min reaction times were the same (within experimental error). It seems that a digestive ripening[16] process led to repeated cycles of dissolution and precipitation that did not dramatically change the particle size but contributed to the porous nature of the product. Thus, it is concluded that the annealing process did not change considerably the porous nature of the prepared materials. It is suggested that 10 min is sufficient to obtain the product. In the next 20 min, the reflux that the solution undergoes leads to a digestive ripening process that is reflected in a higher surface area. Although the exact mechanism is not known, it has been suggested that the digestive ripening involves the dissolution and reprecipitation of the particles. In fact, in a recent MW reaction, Gao *et al.*[17] reduced silver ions in a MW hydrothermal reaction for 3 h. The reduction of silver ions in ethylene glycol usually takes 1–5 min. For Stoeva *et al.*[16], leaving the reaction to reflux for a long time yielded highly organized nanostructures with a narrow size distribution that also resulted in digestive ripening. On the other hand, the surface area of the sonochemical product after calcination at 900° is very small, only 5 m^2g^{-1}, while the nanoYAG with κ-carrageenan sample, after calcination, reaches a value of 21 m^2g^{-1}. This is in accordance with the SEM pictures, demonstrating much smaller particles for the nanoYAG–κ-carrageenan sample.

Conclusions

This paper reports two new techniques for the preparation of nanoYAG particles, *i.e.*, sonochemical and microwave dielectric heating. The advantages of the described processes are their simplicity, their short reaction times and the cheapness of the preparation of the YAG structure. The particles were prepared in nanosizes, and identical particle sizes were measured for the annealed nanoYAG products obtained by both methods. In addition to our attempts, we also repeated the experiment reported in ref. 12. The annealed product was not pure and also contained the YAP phase. Furthermore, the measured surface area was much smaller than that originally reported. According to Wang,[18] the secret lies in the volume of the 5 M ammonia solution used, which has to be large, and is not given in ref. 12. The control experiments, in which sonochemical and MW techniques were not used, led also to the formation of nanoYAG particles, however, they were accompanied by impurities. The absence of impurity phases in the sonochemical and MW experiments might be due to the creation of hot spots in both cases. Thus, although the temperature in the solvent is moderate (100 °C), higher temperatures are created locally in the solvent. Finally, neither the sonochemical nor the MW techniques are major players in the precipitation of the prepared material, which occurs without their application. We attribute the reduction in particle size, compared with the unassisted reaction, to these two methods. Thus, upon annealing, a pure product is obtained, while when the unassisted product is being heated, the YAG contains an impurity phase.

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References

1 X. Guo, P. S. Devi, B. G. Ravi, J. B. Parise, S. Sampath and J. C. Hanson, *J. Mater. Chem.*, 2004, **14**, 1288.
2 M. Veith, S. Mathur, A. Kareiva, M. Jilavi, M. Zimmer and V. Huch, *J. Mater. Chem.*, 1999, **9**, 3069.
3 B. J. Chung, J. Y. Park and S. M. Sim, *J. Ceram. Proc. Res.*, 2003, **4**(3), 145.
4 S. Roy, L. Wang, W. Sigmund and F. Aldinger, *Mater. Lett.*, 1999, **39**, 138.
5 J. W. Nowok and J. P. Kay, *J. Mater. Sci. Lett.*, 2001, **20**, 1331.
6 M. B. Kakade, S. Ramanathan and P. V. Ravindran, *J. Alloys Compd.*, 2003, **350**, 123.
7 B. H. King and J. W. Halloran, *J. Am. Ceram. Soc.*, 1995, **78**, 2141.
8 Y. Liu, Z.-F. Zhang, B. King, J. Halloran and R. M. Laine, *J. Am. Ceram. Soc.*, 1996, **79**, 385.
9 A. M. George, N. C. Mishra, M. S. Nagar and N. C. Jayadevan, *J. Therm. Anal.*, 1996, **47**, 1701.
10 M. Yada, M. Ohya, M. Machida and T. Kijima, *Chem. Commun.*, 1998, 1941.
11 C. J. Harlan, A. Kareiva, D. B. MacQueen, R. Cook and A. R. Barron, *Adv. Mater.*, 1997, **9**, 68.
12 H. Wang, L. Gao and K. Niihara, *Mater. Sci. Eng. A*, 2000, **288**, 1.
13 A. Gedanken, *Ultrason. Sonochem.*, 2004, **11**, 47.
14 R. Harpeness, A. Gedanken, A. M. Weiss and M. A. Slifkin, *J. Mater. Chem.*, 2003, **13**, 2603.
15 R. Harpeness and A. Gedanken, *Langmuir*, 2004, **20**, 3431.
16 S. Stoeva, K. J. Klabunde, C. M. Sorensen and L. Dragieva, *J. Am. Chem. Soc.*, 2002, **124**(10), 2305.
17 F. Gao, Q. Lu and S. Komarneni, *Chem. Mater.*, 2005, **17**, 856.
18 Hongzhi Wang, private communication.