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Synthesis of yttrium aluminium garnet by the citrate gel process

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We describe the synthesis of polycrystalline yttrium aluminium garnet (YAG) by the citrate gel process. The conditions for obtaining the pure phase have been determined and the YAG powders were characterized by X-ray diffraction, IR spectroscopy and transmission electron microscopy. YAG powders were obtained at significantly lower temperatures than by other conventional techniques. Moreover, the particle size of the powders prepared through this process is in the range 20–70 nm, depending on the thermal treatment. The lattice parameter of the YAG powders was also determined and we observed that the lattice parameter depends on the particle size. An explanation for this behaviour is provided.

Yttrium aluminium garnet (YAG), with the chemical composition $Y_3Al_5O_{12}$, is important as an advanced optical material. Single crystals of YAG doped with neodymium are widely used in solid-state lasers. However the obtaining of single crystals of YAG requires complex methods of synthesis. For this reason, in recent years there have been efforts to make polycrystalline YAG powders, which can be pressed into disks and sintered, in order to obtain translucent disks suitable for optical applications.[1] Furthermore, YAG doped with europium or terbium are useful phosphors[2] to prepare high-resolution display devices, which require thin fluorescent screens with fine grain phosphors.[3] Also, YAG doped with samarium thin films could be useful as pressure–temperature sensors.[4] Such thin films could be prepared by spin-coating of a gel. Then, a suitable method to obtain these materials as fine grains or thin films should be developed. Polycrystalline YAG can be prepared by solid-state reaction between Y_2O_3 and Al_2O_3, but high temperatures are required: when the reactants are heated below 1600 °C, a single phase cannot be obtained. YAG has also been prepared by hydroxide coprecipitation[5,6] and by an alkoxide method.[7] This report describes the work carried out in synthesizing YAG using a citrate gel. Previously we used this citrate gel process for the yttrium iron garnet synthesis,[8] and we obtained a pure YIG powder constituted of ultrafine particles, by firing the gel at 650 °C. For early work relating to the synthesis of many oxides by the sol–gel process or by related methods, we refer the reader to ref. 9 and 10. Also a recent review about these methods can be found in ref. 11.

Experimental

Stoichiometric mixtures of nitrates of aluminium(III) (Aldrich, 98%) and yttrium(III) (Aldrich, 99%) were dissolved in an aqueous solution of citric acid (Aldrich, 99%). The prepared solution was 2 M in citric acid, 0.2 M in aluminium nitrate and 0.12 M in yttrium nitrate. This solution was heated at 80 °C in order to obtain a gel, and the gel was dried at 110 °C for 36 h and further heat-treated in air at temperatures between 800 and 1100 °C, with a heating rate of 10 °C min^{-1}. These conditions were determined to be the best for the yttrium iron garnet synthesis,[8] and we found that they are also very suitable for the YAG synthesis. A scheme of the preparation method is shown in Fig. 1 and the samples prepared as well as their thermal treatment are summarized in Table 1.

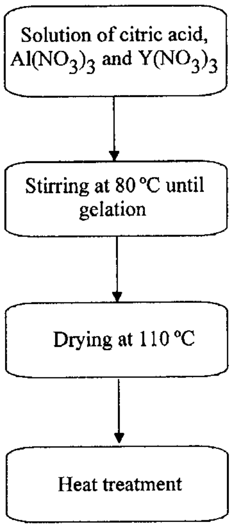

Fig. 1 Schematic representation of the synthesis process

Samples were characterized by X-ray diffraction (XRD) using a Philips PW-1710 diffractometer equipped with a Cu anode (Cu-Kα radiation). The different phases were identified using the JCPDS Powder Diffraction Files.[12] The mean particle size and the microstrains were estimated with the single line method,[13] assuming a Lorentzian shape for the size broadening and a Gaussian shape for the microstrain broadening. Calculations were performed over the line (420). Instrumental width was determined with a YIG (yttrium iron garnet) specimen prepared by the ceramic method, which had large crystallites and was free from defect broadening, and the diffraction peaks were fitted by a pseudo-Voigt function, using the program XRFIT.[14] We used a YIG specimen as standard owing to the high temperatures required to obtain a pure YAG specimen by solid-state reaction. Lattice parameters were determined with the program XLAT.[15] IR spectroscopy measurements were recorded with a Bruker IFS 66 V instrument using the KBr pellet method. A transmission electron microscopy (TEM) study was performed with a Philips CM-12 microscope. The specimens for TEM were obtained by ultrasonically dispersing the particles in water and depositing drops of this suspension on a grid covered with Formvar.

Results and Discussion

The XRD pattern of the sample prepared by heating at 800 °C does not exhibit any Bragg lines, only a broad band centered

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Table 1 Thermal treatment of the samples and their mean particle size, determined by XRD and TEM measurements

sample	treatment temperature/°C	treatment time/h	XRD size $\langle D\rangle_v$ (420)/nm	TEM size mean length/nm	standard deviation/nm	TEM size mean width/nm	standard deviation/nm
A	800	2	—	—	—	—	—
B	900	2	20	32	8	15	4
C	950	2	27	—	—	—	—
D	1000	2	34	—	—	—	—
E	1100	2	53	73	22	34	8
F	1100	12	70	—	—	—	—

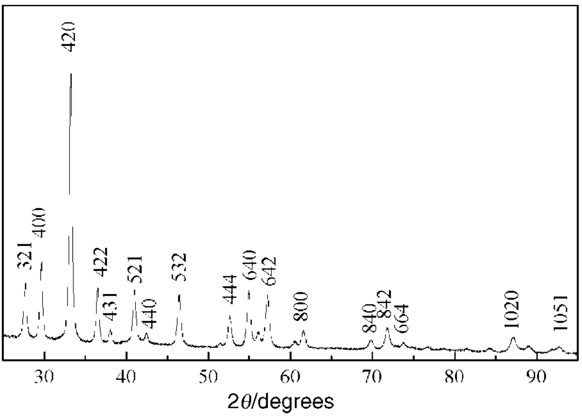

Fig. 2 XRD pattern of sample C

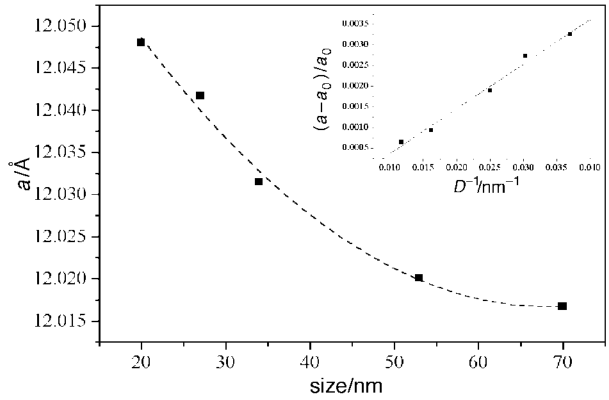

Fig. 4 Dependence of the lattice parameter on the mean particle size

at 31° (2θ), therefore we concluded it is amorphous. When heated above 800 °C, samples fully crystallize and contain YAG as single phase (see Fig. 2); no other phases were detected. It must be emphasized that this synthesis temperature is significantly lower than those required by solid-state reaction (>1600 °C). From these XRD patterns one can observe that peaks are quite broadened, owing to the small crystallite size and/or microstrains. Previously to the single-line method analysis, we made Williamson–Hall plots[16] for the XRD patterns of the crystallized samples. Such a plot gives a line with positive slope if the specimen exhibits microstrain and a non-zero intercept if the specimen exhibits size broadening. Our samples exhibit both a non-zero intercept and a positive slope, therefore we conclude that broadening is due to both size and microstrain effects. Hence, we applied the single-line method in order to determine the crystallite size and the microstrains for these samples. We obtained that the mean crystallite size varies over the range 20–70 nm, depending on the conditions of thermal treatment (see Table 1). Increasing the temperature or the treatment time of the samples, the mean crystallite size increases and microstrains decrease.

A TEM study was performed on the samples B and E. Fig. 3 shows a typical TEM image of the sample E. In all the studied samples, particles exhibit generally lengthened rounded irregular shapes. The mean particle width and length were estimated from the TEM images by sampling different areas. The obtained values, as well as their standard deviations for a Gaussian distribution, are summarized in Table 1. These results are in good agreement with the crystallite sizes estimated from the X-ray line broadening measurements and we can conclude, therefore, that every particle contains one crystallite. Moreover we found that these particles are similar to those of YIG prepared by us,[8] and consequently we do not present here a detailed study by HREM.

The lattice parameter values of these samples are larger than that of ceramic YAG ($a = 12.0089$ Å, JCPDS 33–40). Furthermore, the increase in time or temperature of the thermal treatment leads to specimens with lattice parameters closer to those of the ceramic material. We observed also a dependence of the lattice parameter on the mean particle size of the samples (see Fig. 4). Similar behaviour has been reported for small particles of other materials.[17–19] As a general rule, nanoparticles of oxides exhibit a lattice expansion with reduction in particle size while metal particles exhibit a lattice contraction. On the inset of Fig. 4 is shown a plot of $(a-a_0)/a_0$ *vs.* the reciprocal

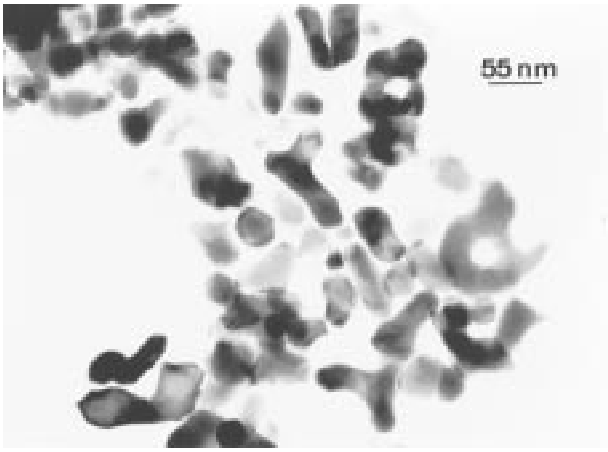

Fig. 3 TEM image of sample E

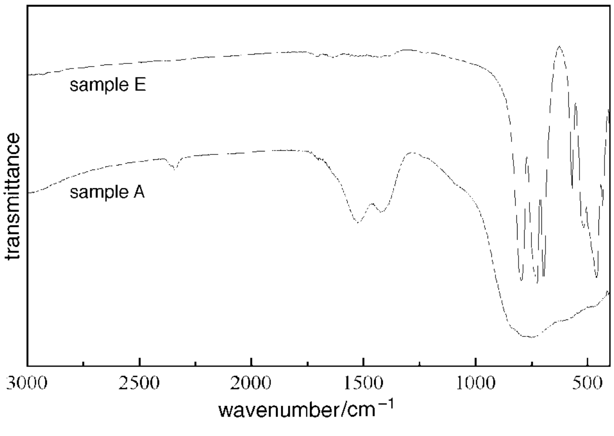

Fig. 5 IR spectra of samples A and E

Table 2 Comparison of IR vibrational frequencies of sample E and YAG powder absorption data[25]

sample E (ν/cm^{-1})	YAG (ν/cm^{-1})	sample E (ν/cm^{-1})	YAG (ν/cm^{-1})
794	789	388	389
727	726	375	376
694	691	329	330
569	567	290	290
—	532	220	220
516	522	178	179
461	463	166	167
432	432	122	121
—	396		

of the mean particle size, where a_0 is the lattice parameter of bulk yttrium aluminium garnet. It can be seen that $(a-a_0)/a_0$ increases with decreasing size and this increase is inversely proportional to the particle diameter. This dependence could be expressed as:

$$\frac{(a-a_0)}{a_0}=\frac{A}{D}$$

where D is the particle diameter and A is the slope of the straight line. The reciprocal of the diameter (D^{-1}) is proportional to the surface to volume ratio (S/V) and consequently, the increase of the lattice parameter can be related to the higher surface to volume ratio in the smaller particles, resulting in a higher contribution from the surface layer. In oxide particles, the bonds have a directional character and at the outer surface of each particle, there would be unpaired electronic orbitals, which would repel each other.[20] This contribution from the surface layer increases with decreasing particle size and leads to larger values of the lattice parameter than in the bulk. The resulting behaviour is sometimes compared to that observed by applying an 'equivalent negative pressure',[21] which arises from the increase of the repulsive dipolar interactions at the surface. However, some authors[22] have attributed the lattice expansion with decreasing particle size to an increase in vacancy or impurity concentrations. According to Gamarnik,[23] such an explanation is not convincing because there is no direct information which can confirm the increase of impurities or vacancies.

The IR spectrum of the sample heated at 800 °C exhibits two bands at 1520 and 1400 cm^{-1}, assigned to carbonates.[24] Moreover, there is a weak band at 2340 cm^{-1}, assignable to CO_2, and a broad band at 700 cm^{-1}, assigned to the vibrations of Al—O (see Fig. 5). IR spectra of the samples heated above 800 °C exhibit the characteristic bands of YAG. Table 2 compares the IR spectral data of the sample E and polycrystalline YAG,[25] which show good agreement. In our spectra we observed also some very weak bands around 1500 cm^{-1}, which could be assignable to carbonates.

Conclusions

Using the citrate gel process we can obtain pure polycrystalline YAG at substantially lower temperatures than using the ceramic method as well as other wet methods. Furthermore, no other phases, such as $YAlO_3$ or $Y_4Al_2O_9$, were detected. Our YAG powders are constituted by ultrafine particles whose mean size range from 20 to 70 nm depending on the thermal treatment. Upon decreasing in particle size a lattice expansion occurs. To our knowledge an increase of the lattice parameter of YAG small particles with decreasing their size has not been reported in the literature up to now. We provide a tentative explanation of this behaviour on the basis of an increase of the repulsive dipolar interactions at the surface of the particles, but in order to exclude the hypothesis of an increase in impurities or vacancies, further studies should be done.

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