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Preparation of $Y_3Al_5O_{12}$ Nanocrystals by a Glycol Route

Kunwar Singh Bartwal,*,† Sujan Kar,** Nanda Kaithwas,*** Monica Deshmukh,*** Mangla Dave,*** and Hojin Ryu***

**Advanced Materials Division, Korea Research Institute of Chemical Technology, Daejeon 305-600, Korea*

***Laser Materials Development and Devices Division, Raja Ramanna Centre for Advanced Technology, Indore 452013, India*

****Halkar Science College, Indore 452 001, India*

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ABSTRACT

Yttrium aluminum garnet, $Y_3Al_5O_{12}$ (YAG) is an extensively used solid-state laser host material. YAG nanocrystals were synthesized using low-temperature glycol method, a modified sol–gel method performed at low temperature that consists of a mixture of salts that are mostly nitrates in an aqueous media. Single-phase nanocrystalline YAG was obtained at 850°C, which is a much lower temperature than with other techniques such as a wet-chemical technique. The structural characterization is done by powder X-ray diffraction, scanning electron microscopy and transmission electron microscopy. A crystallite size range of 20-50 nm was observed for the materials prepared at 850-950°C.

Key words*: *Nanocrystals, $Y_3Al_5O_{12}$, X-ray diffraction, Electron microscopy, Sol-gel preparation

1. Introduction

Yttrium aluminum garnet, $Y_3Al_5O_{12}$ (YAG), is a well-known laser host inorganic material. It has excellent chemical, physical and optical properties that make it suitable for many optical device applications. The single crystals of YAG have been drawing considerable attention since the early 1960s for their fluorescence and solid-state lasers applications. YAG materials have been widely studied in the application of displays because of their stability under conditions of high irradiance with an electron beam. YAG is used as the host material of full-color phosphors with various doping materials including Ce, Tb, Eu, and Tm. YAG single crystals doped with lanthanides such as Nd^{3+} and Er^{3+} are used in solid-state lasers, and polycrystals of YAG doped with different color centers are employed as phosphors in cathode ray tube (CRT) displays.[1,2] YAG materials, which are mainly used in powder form, are prepared conventionally by solid-state reactions using yttria (Y_2O_3) and alumina (Al_2O_3) compounds. Often several stable phases of $YAlO_3$ (YAP) and $Y_4Al_2O_9$ (YAM) are formed as intermediate products of YAG particles in solid-state reactions. This process involves extensive heat treatments at high temperatures (>1800°C) and repeated mechanical mixing to achieve a pure garnet structure. Due to insufficient mixing and the low reactivity of the raw materials, YAM and YAP exist in the products.[3] There are several reports involving the fabrication of YAG ceramics due to their enhanced optical and mechanical properties.[4,5] In an effort to overcome the drawbacks of the solid-state reaction process, several wet-chemical methods such as co-precipitation,[6,7] combustion,[8] and spray pyrolysis[9] have been developed to fabricate YAG-based phosphors. Although YAG can be obtained at low temperatures via these methods, further annealing at high temperatures (>1400°C) is required to improve the luminescent properties of the powders. Recently, a sol–gel process using metal alkoxides was used for synthesizing YAG phosphor ceramics.[10] However, this process is complicated due to the difficulty with the handling of the alkoxides involved. Several attempts have been made to prepare YAG ceramics in nanocrystalline form to overcome the drawbacks of the high-temperature sintering associated with these garnets.[11-13] The lowest temperature for annealing (~700°C) was found for single-phase YAG powder made via an alkoxide sol–gel mixture technique.[14,15] It has been well demonstrated that the sol–gel method has the considerable advantages of the proper mixing of the starting materials as well as good chemical homogeneity of the product. However, this method is very sophisticated series of treatments for the alkoxides are necessary to avoid the presence of metastable $YAlO_3$ up to 1200°C in addition, there is the high cost of the precursors.

In this paper, the synthesis of nanocrystalline YAG at 850°C using a modified glycol method is reported. This involves a reasonably low temperature for processing nanocrystalline YAG. The annealed YAG powder was characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques to establish a single phase and the

†Corresponding author : Kunwar Singh Bartwal
E-mail : bartwalks@yahoo.co.in
Tel : +82-42-860-7376 Fax : +82-42-861-4245

specified size of the crystallites.

2. Experimental

There are several reports on the preparation of this material using a solvo-thermal method. However, the present technique is based on the simple mixing of low cost nitrates as a precursor and chemical mixing with the help of ethylene glycol at a very nominal temperature in the range of 70-80°C. The ethylene glycol assists in the formation of a corresponding alkoxide, which becomes easily mixed at an atomic scale, forming the required compounds. This technique is some time also referred to as a modified sol-gel method. The annealing temperatures required to obtain the YAG nano crystals are sufficiently low (~850-900°C). The present technique is thus cost effective and simple to perform. $Al(NO_3)_3 \cdot 9H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ were used as starting materials. An aqueous solution of $Y(NO_3)_3$ was prepared in 100 ml of CO_2 free distilled water premixed with 2 ml of acetic acid (CH_3CO_2H). This mixture was stirred for 2-3 h at a temperature ~50°C. In another beaker, the aluminum nitrate $Al(NO_3)_3 \cdot 9H_2O$ was dissolved in 50 ml of CO_2 free distilled water and stirred for 1-2 h at room temperature. After completion of the stirring, both solutions were mixed in a single beaker with 2 ml of 1, 2-ethanediol (ethylene glycol) and stirred again. The resulting colorless solution was stirred at 70-80°C to evaporate all the solvents slowly until a foam was formed. This drying process is critical and can often require several hours to complete. The foam was slowly dried at 120°C and then ground in an agate mortar to obtain a fine powder. This dirty white powder was annealed at 700°C for 5-6 h raised to 800°C for 12 h and then raised successively to 850, 900 and 950°C for 4-5 h for each run. Powders annealed at different temperatures were taken for the XRD experiments. Powder XRD were taken on Rigaku Geiger Flex X-ray diffractometer with CuK (=1.54178 Å) radiation. The samples were scanned for 2θ values from 20 to 70 and 0.05 steps. The powder annealed at 900°C and 950°C was used for the SEM and TEM experiments. The sample for the TEM observation was prepared by suspending the particles in methanol by ultrasonification and drying a drop of the suspension on a carbon-coated copper grid. TEM was carried out with a Philips Tecnai G2-20 (FEI) machine operating at 200 kV.

3. Results and Discussion

The YAG crystal belongs to the cubic structure with a =1.2010 nm; it is in the Ia3d space group. It is well known that only pure YAG phase is favorable for the luminescent properties of phosphors, but this normally requires a high temperature close to 1600°C to synthesize the pure YAG phase via the solid-state reaction of Al_2O_3 and Y_2O_3. Impure phases such as YAP (polymorphs structure) and YAM (monoclinic structure) frequently coexist with the YAG (cubic structure) phase. Powders annealed at different temperatures were tested sequentially in terms of their phase and crystallinity.

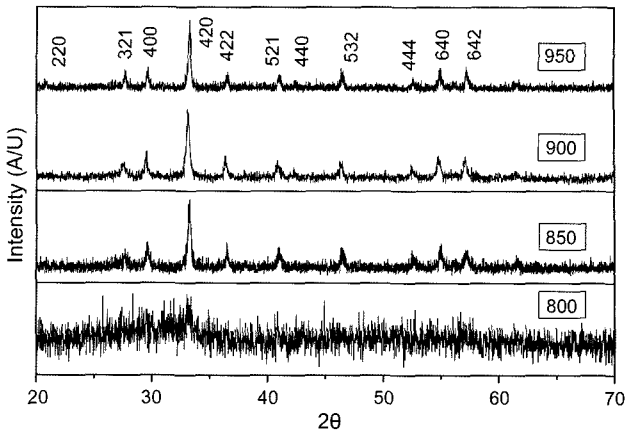

Fig. 1. XRD patterns of YAG nanocrystals at various annealing temperatures.

Fig. 1 shows the XRD patterns for nanocrystalline YAG powders annealed at different temperatures. It is clear from the XRD patterns that the powder annealed at 800°C is amorphous but has started showing the faint peaks of a single crystal phase. It can be observed that the powder annealed at 800°C is characterized as having a non-crystalline structure (short- range order) or a small crystallite size (less than 5 nm) which can be considered YAG embryos. As the powder was annealed at 850°C the crystalline peaks appeared with good intensity. The curves taken at 900 and 950°C are again with the complete crystalline structure with a single phase. However, the grain size began to increase with a higher annealing temperature as was expected. The well-resolved peaks perfectly match the JCPDS data on YAG crystals. The lattice parameter calculated is a = 12.025 Å with a cubic structure of the Ia3d space group. It is expected that upon annealing the crystallite size will grow and the cell parameters and (consequently) the cell volume will decrease linearly with the annealing temperature. The cell parameters reported in JCPDS (cubic) for YAG crystals correspond to the bulk value of a_0= 12.010 Å Shrinking has been reported in the cubic cell parameter of YAG from 12.037 Å to 12.010 Å, as the annealing temperature increased.[15] This could be explained in terms of the existence of non-bridging oxygen O_{nb}, which disappears with the annealing process. The existence of O_{nb} is essentially an oxygen deficiency that is enhanced by the high surface/volume ratio of the nanocrystals. These vacancies expand the lattice parameter due to the deformation of the crystalline network without changing the basic crystal structure. The crystallite size of the sample annealed at a temperature >1000°C is in the limit of the accepted size for nanocrystals and the cell parameter is similar to the value reported for a YAG monocrystal.[16] There is no signature for the presence of any secondary phase in the powder. From X-ray diffraction patterns, the effective crystallite size (particle size) was calculated based on the line-broadening of the XRD peaks.

The use of the Voigt function for the analysis of the integral breadth of the broadened X-ray diffraction line profile forms the basis of a rapid and powerful single line method of crystallite size and strain determination. In this case, the constituent Couchy components can be obtained from the ratio of the full-width at half maximum intensity (2ω) and the integral breadth (β). In a single line analysis the apparent crystallite size 'D' can be related to the Couchy (β_c) width of the diffraction peak at the Bragg angle θ;

Crystallite size "D"$=\lambda/\beta_c \cos\theta$

The constituent Couchy components can be given as

$\beta_c=(a_0+a_1\psi+a_2\psi^2)\beta$

Here, a_0, a_1 and a_2 are Couchy constants and $\psi=2\omega/\beta$ where β is the integral breadth obtained from the XRD peak. The values of the Couchy constant were taken from the table of Langford for the relevant crystal system. Incorporating these values the crystallite size D was calculated, and was found to be in the 20-50 nm range.

The SEM study was carried out to know the average particle size of the nanocrystals and the morphology. The powder samples synthesised at temperature between 850-950°C were utilized for these experiments. Figs. 2 (a, b, and c) show SEM micrographs taken of YAG nano crystals at different annealing temperatures. It is clearly seen from these micrographs that the crystallites sizes vary with the annealing temperature. The sizes are in the range of 30-50 nm. As the temperature rises above 900°C the agglomeration along with the nano crystallites can be seen.

A TEM study is the best tool to use in order to understand the local structure and the particle size of nanocrystals. TEM studies were conducted to investigate the morphology and the size of the YAG nanocrystals. The powder samples synthesised at temperature 850-950°C were used for these experiments. Figs. 3 (a, b, and c) show TEM micrographs

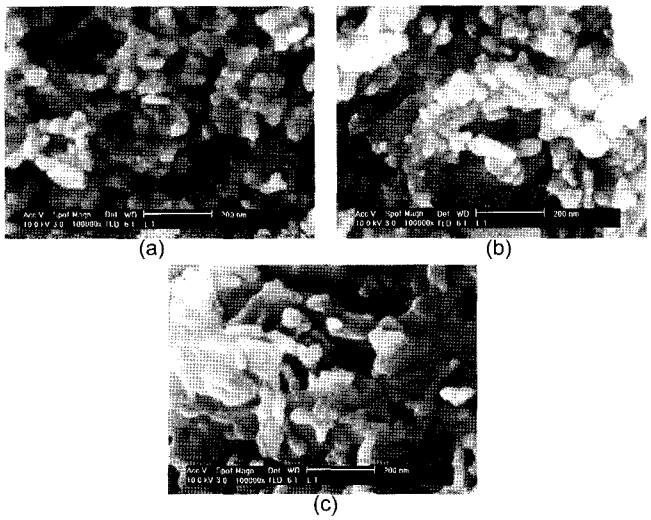

Fig. 2. SEM micrograph of YAG nanocrystals (a) 850°C, (b) 900°C, and (c) 950°C.

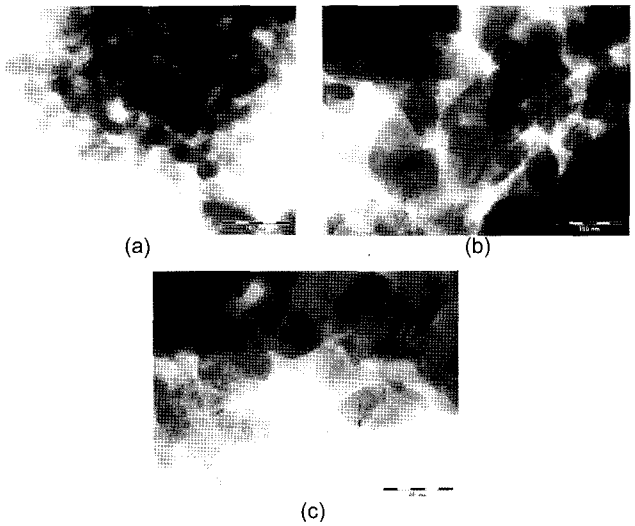

Fig. 3. TEM micrograph of YAG nanocrystals (a) 850°C, (b) 900°C, and (c) 950°C.

taken for samples annealed at different temperatures. When the annealing temperature is higher than 850°C the YAG particles grow and form an agglomeration. These agglomerations are clearly visible in these micrographs. These micrographs show that the nanocrystals are formed via an agglomeration and that they have sizes 25-50 nm depending upon the annealing temperature. The micrograph also suggests that the nanocrystals are mostly of the same size for a particular annealing temperature. It should be noted that the size of the YAG crystallites annealed at 850°C is approximately 20-25 nm. When the temperature rose to 950°C the particle size was 40-50 nm and a number of large particles are larger than 50 nm. Fig. 4 shows representative selected area diffraction (SAD) patterns taken for the polycrystalline samples annealed at 900°C. The pattern clearly shows that the sizes of the particles are within a few nanometers of each other. The presence of spots and rings shows the presence of crystallite of a reasonably sufficient size to diffract. The connecting rings indicating the short range order within these crystallites show that the sizes are small for some of the crystallite which further indicates

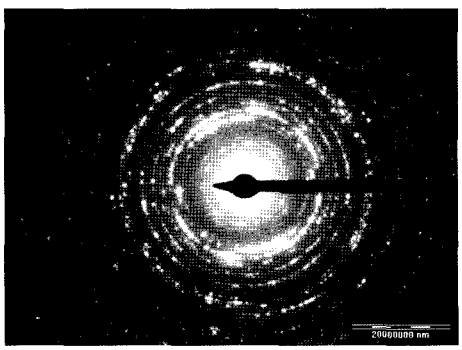

Fig. 4. Representative selected-area electron diffraction pattern of YAG nanocrystals (annealed at 900°C).

the amorphous-like behavior.

4. Conclusions

YAG nanocrystals were synthesized successfully using a low-temperature glycol method. A phase analysis showed single-phase nanocrystalline YAG was obtained at 850°C, a temperature much lower compared to other techniques such as a wet-chemical technique. This method is much simpler and more cost effective compared to the alkoxide sol–gel process. The TEM results show that the typical crystalline sizes depend on the annealing temperature. The sizes were determined to be in the range 20-50 nm. Agglomeration of these nanocrystallites was observed as the annealing temperature increased.

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