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Rapid synthesis of Nd:YAG nanopowder by microwave flash combustion

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Nd:YAG nanopowders were successfully synthesized by a novel approach using rapid microwave drying of sol. Citrate nitrate sol was treated in a microwave oven for a few minutes. The as-prepared precursor was calcined at 900 °C for 2 h. Characterization was done by thermogravimetric analysis, Fourier transform infrared spectroscopy, X-Ray diffraction (XRD) and transmission electron microscopy (TEM). XRD showed the formation of phase pure polycrystalline YAG. The particle size was found to be 24 nm (estimated from Scherrer's equation). TEM indicated that the particle size was in the 24–70 nm range. Nd^{3+} doping was confirmed by SEM–EDX. Nd:YAG nanopowder synthesized by this method was of low agglomeration and the particles were spherical in shape.

Key words: *microwave-flash combustion; Nd:YAG; nanopowder; transparent ceramics*

1. Introduction

Yttrium aluminum garnet, $Y_3Al_5O_{12}$ (YAG), is a well-known inorganic compound with excellent chemical, physical and optical properties. The usual applications of nanosized YAG doped with lanthanide ions include phosphors and laser active media [1]. Recent investigations indicate that Nd:YAG polycrystalline ceramics based on the sintering of nanopowders are one of the most promising materials for solid state lasers [2–6]. There are several methods to produce Nd:YAG nanopowder such as the sol-gel method [7, 8], co-precipitation [9, 10], spray pyrolysis [11] and the combustion [12, 13] technique. Microwave assisted processing is an area of recent research into the rapid and controlled synthesis of homogeneous nanopowders which have low sintering temperature, high density and an improved microstructure for the fabrication of transparent ceramics [14]. It has been claimed that this route can produce materials with superior properties compared with those fabricated by conventional methods [15].

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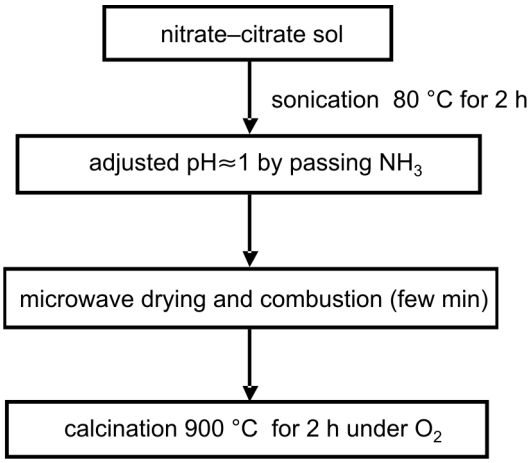
In a microwave combustion process, since the heating takes place at the molecular level, such a process is likely to produce less agglomerated powders than those reported for other materials [16] In this paper, we report on the synthesis of Nd:YAG nanopowders by the microwave induced combustion reaction. Microwave initiated combustion has several advantages, such as rapid heating and enhanced reaction kinetics [17].

2. Experimental

Aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$ (99.9% purity Alfa Aesar), yttrium nitrate, $Y(NO_3)_3 \cdot 6H_2O$ (99.9% purity Alfa Aesar), neodymium nitrate, Nd $(NO_3)_3 \cdot 6H_2O$ (99.9% purity Alfa Aesar) and citric acid anhydrous (99.5% purity Alfa Aesar) were used as-provided to prepare Nd:Y:Al in the molar ratio of 0.06:2.94:5. This was subsequently dissolved in water so as to achieve a total solid content of 60%, after the addition of citric acid. Water for preparing the solutions was purified using a Millipore Elix 10 purifier. The nitrate–citrate sol was sonicated for 2 h at 80 °C in an ultrasonic bath having the frequency of 40 kHz (Scheme 1). pH was then adjusted to ca. 1 by passing dilute gaseous ammonia. The sol was transferred into an alumina crucible. Drying was carried out using a 2.45 GHz domestic microwave oven at 900 W, till combustion took place. Combusted powder was calcined at 900 °C for 2 h in an oxygen rich atmosphere, maintained by passing oxygen gas (3 dm^3/min). The heating rate, from room temperature to 900 °C, was maintained at 10 °C/min using a Eurotherm 2604 microprocessor controlled temperature programmer.



Scheme 1

TG/DTA of combusted powder was carried out in air at the heating rate of 10 °C/min from room temperature to 1300 °C, on a Perkin Elmer Diamond simultaneous TGA/DTA system. FTIR spectra were recorded with a FTIR Spectrometer (Bruker, model Vector 22) using KBr pellets. XRD was carried out using a Philips X-ray dif-

fractometer, PW 3020 in the 2θ range from 15° to 80°, keeping a step size of 0.02. Particle size was calculated using Scherrer's equation [18]:

$$p = \frac{0.9\lambda}{(\beta^2_{\text{sample}} - \beta^2_{\text{inst}})^{1/2} \cos\theta} \tag{1}$$

where p is the crystallite diameter, λ = 1.54056 Å, θ is the diffraction angle, β_{sample} is the full width at half maximum (FWHM) of the diffraction peak and β_{inst} is a characteristic parameter of the instrument. Nd^{3+} doping was confirmed by EDX using a scanning electron microscope (Zeiss Evo Series 50). The particle size and the morphology of the crystalline powder was characterized by Transmission Electron Microscope (FEI Philips Morgagni 268D, AC Voltage 100kV having a magnification factor of up to 280,000)

3. Results and discussion

The thermal analysis of microwave combusted precursor of Nd:YAG powder is shown in Fig. 1. The first weight loss, for temperatures of up to 200 °C, is due to the dehydration of adsorbed moisture. Weight loss for temperatures between 350 to 550 °C is due to the loss of organic residues, in the form of carbon dioxide, and the decomposition of nitrates. A total weight loss of ~62% was observed for temperatures of up to 550 °C. An exothermic peak at ~ 934 °C, along with small weight loss, is due to the crystallization of YAG. X-ray diffraction shows that under isothermal heat treatment conditions the crystalline phase appears even at a much lower temperature [19, 20].

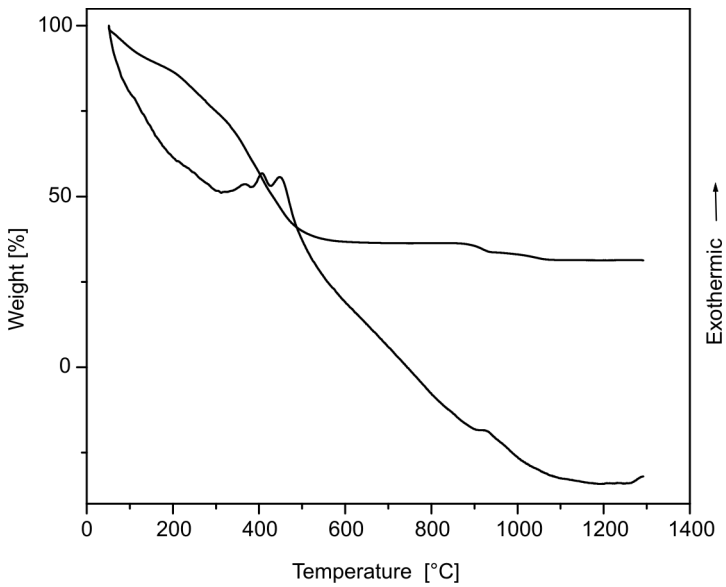


Fig. 1. TGA and DTA curves of Nd:YAG precursor powder by the microwave flash combustion technique

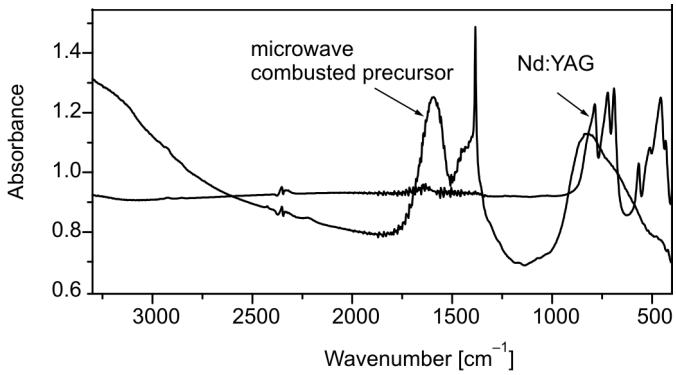


Fig. 2. FTIR of microwave combusted precursor and Nd:YAG powders

FTIR spectra in Fig. 2 show a band at ca. 2350 cm^{-1}, which belongs to carbon dioxide from the atmosphere. The inequalities in the path length in the spectrometer result in an imperfect subtraction of sample and reference beams, and thus the peak attributed to atmospheric carbon dioxide appears in the spectrum [21, 22]. The broad band in the region of 900–450 cm^{-1} in a precursor is replaced by several bands. The FTIR spectrum of the microwave combusted and calcined powder Nd:YAG exhibited well defined peaks at 787, 722 and 690 cm^{-1}, due to stretching vibrations of the Al–O bond in tetrahedral sites, and absorption peaks at 566, 511, 457 and 432 cm^{-1} associated with stretching of the Al–O bond in octahedral sites of the garnet structure. The peaks matched with the reported data for a well crystallized YAG [23, 24].

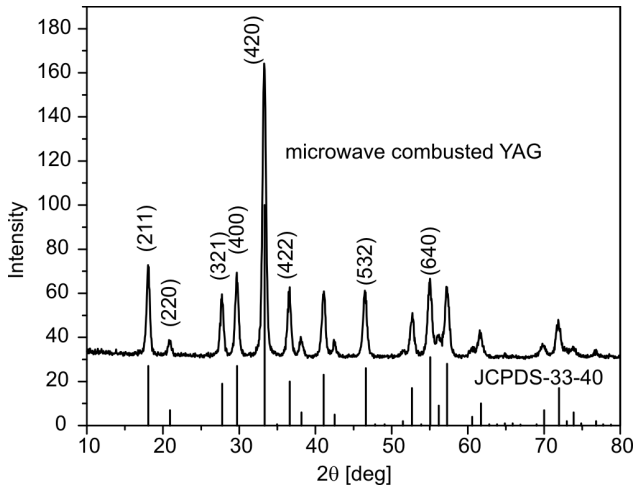


Fig. 3. XRD pattern of nanocrystalline Nd:YAG powder calcined at 900 °C for 2 h under oxygen atmosphere

The peaks observed in the XRD pattern for the powder calcined at 900 °C for 2 h in an O_2 atmosphere are shown in Fig. 3. XRD peaks were indexed in terms of the

garnet structure, according to standard JCPDS 33-40. The main peak is centred at 2θ = 33.35° and corresponds to a crystal plane with Miller indices of [420] characteristic of YAG [24]. The average primary particle size, calculated from Scherrer's equation, was 24 nm. The cell parameter calculated by the least square method was found to be 12.026 Å for microwave synthesized Nd:YAG, indicating partial substitution of Y^{3+} sites with Nd^{3+} cations [21, 26]. The cell parameters reported in JCPDS for YAG (cubic) crystals is 12.010 Å [27].

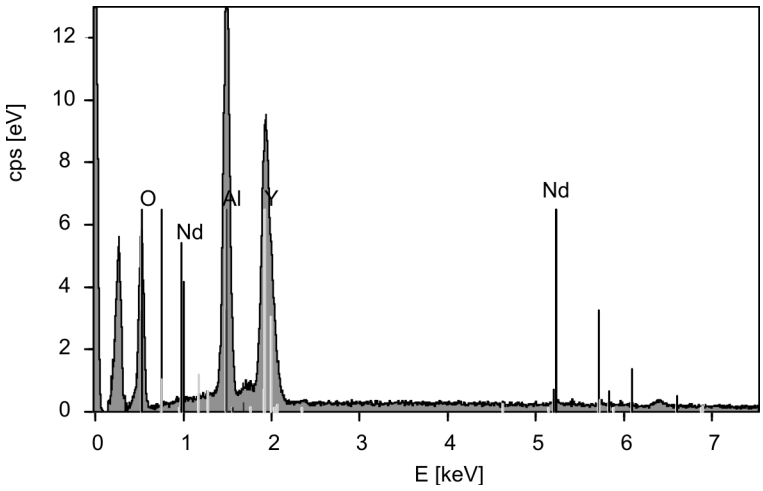


Fig. 4. EDX spectra of calcined Nd:YAG powder

EDX powder spectra in Fig. 4 confirmed the doping of Nd^{3+} ions. Peaks of all constituent elements Y, Al, Nd and O are observed in the EDX spectrum of Nd:YAG nanopowders.

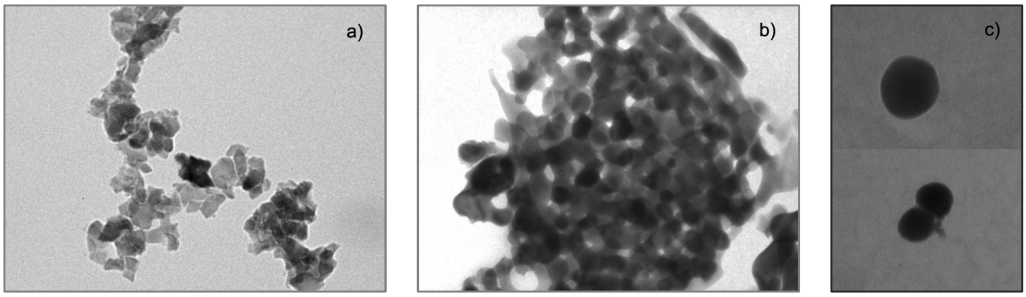


Fig. 5. TEM images of Nd:YAG powder synthesized by:
a) conventional sol-gel method and b), c) using microwave heating

The TEM micrographs of Nd:YAG powder calcined at 900 °C for 2 h in an oxygen atmosphere are shown in Fig. 5. The particle size was observed in the range of 24–70 nm. The shape of the particles was spherical and regular compared with that of

particles prepared by the conventional, but otherwise similar, sol-gel process (Fig. 5). Particles were found to be separate and less agglomerated. Microwave assisted synthesis mostly yields less agglomerated powder [14]. Such regular shaped spherical nano-sized powders with lesser agglomeration are considered highly sinterable for transparent ceramics [1].

4. Conclusions

Single phase nanocrystalline Nd:YAG powder was synthesized by rapid microwave drying and combustion of nitrate–citrate sol, followed by calcination at 900 °C for 2 h in an oxygen atmosphere. Particle size was found to be 24 nm by XRD. The cell parameter was calculated to be 12.026 Å and SEM-EDX indicates Nd doping.

TEM shows the spherical morphology of nano-sized powders in the range of 24–70 nm, with little agglomeration, indicating higher sinterability.

Microwave processing of sol leads to a fine-grained product in short processing time which makes this process attractive and interesting.

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