Optical Materials 35 (2013) 740–743

Contents lists available at SciVerse ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Sol–gel synthesis and characterizations of crystalline $NaGd(WO_4)_2$ powder for anisotropic transparent ceramic laser application

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ARTICLE INFO

Article history:
Available online 11 October 2012

Keywords:
Transparent ceramics
$NaGd(WO_4)_2$
Nanocrystalline powders
Sol–gel
FE-SEM
Raman

ABSTRACT

$NaGd(WO_4)_2$ powders were synthesized at different pH (3.5, 4.5, 5.5, 6.5 and 7.5) values by conventional Pechini method. Sodium and gadolinium nitrate salts and ammonium paratungstate are used as starting precursors. Metal cations were chelated by citric acid and individual citrates were bound together with ethylene glycol. Synthesized gel was analyzed using differential thermal analysis (DTA), thermo gravimetric (TG) and FT-IR spectroscopy to understand the degradation of gel and formation of metal citrates. Calcined powders (250, 600, 700 and 800 °C) were characterized by powder XRD, FT-IR, Raman and FE-SEM analysis. The temperature dependent phase formation was examined by powder XRD. The morphological changes at different pH derived powders were observed with FE-SEM micrographs. Stepwise organic liberation with respect to temperature and presence of carbon content in the pre-fired powder were analyzed using FT-IR analysis. Raman spectrum reveals disordered tungstate vibrations in the NGW matrix.

1. Introduction

Recent research was focused on alkali rare-earth double tungstate and molybdate compounds for laser and phosphor host applications [1–4]. Among these tungstates, sodium based double tungstates have less destructive phase transition than potassium based double tungstates and does not exhibit a polymorphic phase transformation below their melting point [5]. Tetragonal $NaGd(WO_4)_2$ (NGW) is one of the best upconversion and ultra short pulse laser materials. In NGW matrix, Na^+ and Gd^{3+} are randomly arranged and form a disorder structure. Rare-earth ions can be doped in the NGW lattice with replacing Na^+ (or) Gd^{3+} sites and form an identical S_4 local symmetry [6]. NGW exhibits congruent melting and can be grown by Czochralski method. Formation of cracks at different stages of crystal growth due to anisotropy in thermal expansion coefficients and cleavage plane (001), gas bubble formation during growth, relatively very high melting point, non-uniformity in dopant distribution and economically high cost of growth equipments [7] are some difficulties encountered during melt growth of these crystals.

To overcome these difficulties, recent research has been progressed on preparation of transparent ceramic material with similar properties of single crystals for lasing applications [8,9]. Nanocrystalline powders and novel sintering methods allow much better transparency and high scalability to the transparent ceramics towards high power laser applications. Many cubic nanopowders were prepared for the fabrication of commercial ceramic laser host materials [10]. Earlier reports on ceramic materials highlight on the cubic phase of the particles and new attempts were focused on non-cubic ceramics with highly oriented grains under high magnetic flux [11]. Eventhough it is a tough task, many researchers concentrate on preparing sub-micron particles for preparation of non-cubic transparent ceramics. Synthesis of NGW powder was already reported using hydrothermal method [12]. The present work was concentrated on preparation of micron and sub-micron structured NGW powders using sol–gel method and the effect of pH on morphology of the particles. Synthesized powders were characterized with structural, optical and morphological analysis.

2. Synthesis of crystalline powders

The starting precursors i.e. $NaNO_3$, $Gd(NO_3)_3$ and ammonium para tungstate (analytical grade) were dissolved in 50 ml of deionised water separately. Citric acid was mixed individually in the solution of nitrates and tungstates. After mixing of individual citrates, the mixed solution was stirred for 45 min. Ethylene glycol was then added in the homogenously mixed citrate solution to polymerize the individual citrate complex. The total pH values of the solution were adjusted to 3.5, 4.5, 5.5, 6.5 and 7.5 by adding ammonia solution. This mixed aqueous solution was heated at 80 °C to enhance the polyesterification reaction [13,14]. Gel was formed after complete evaporation of the liquid species present

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http://dx.doi.org/10.1016/j.optmat.2012.08.018

in the solution and temperature of the gel was gradually increased to 110 °C (5 h) for further drying. Dried gels were pre-fired at 250 °C (30 min) in resistive heating furnace. The pre-fired powders were further calcined at 600, 700 and 800 °C at the rate of 60 °C/h.

3. Results and discussion

Thermal analysis (TGA and DTA) were carried out for 3.5 pH derived NGW gel (Fig. 1) using TA instruments, Model: Q600 SDT and Q20 DSC. Formation of NGW consists of two stages of weight loss. In the first stage, 10% of weight loss was observed in the temperature range between 25 and 194 °C. In this region, three endothermic peaks at 54, 91 and 131 °C in DTA reveals the dehydration of residual water and ammonia in the gel. In the second stage, major weight loss of about 64% was observed. Strong exothermic peaks at 224, 248 and 305 °C in DTA in these region can be attributed to the release of high amount of heat due to the decomposition of citrate–ethylene glycol polymeric net. Above 350 °C, no abrupt weight loss (only 6% wt) was observed.

The powder XRD analysis of the as synthesized gel, pre-fired and three different temperature calcined samples were carried out using Philips PW1710 diffractometer with Cu Kα radiation (λ = 1.5406 Å) and are shown in Fig. 2. The pattern corresponding to the gel indicates the amorphous nature of the sample with very low intense unidentified bunch of peaks at around 30°. The powder reflections of pre-fired sample (250 °C) shows the tetragonal phase of NGW (JCPDS Card PCPDF No: 25-0829) with space group $I4_1/a$ and its lattice parameter values are $a = b = 5.243$ Å, $c = 11.384$ Å, $\alpha = \beta = \gamma = 90°$ [15]. The X-ray diffraction indicate, increase in intensity counts for samples calcined at higher temperature. The peaks are sharper due to increase in its crystallinity. The XRD pattern of different pH derived samples calcined at 800 °C shows similar patterns (Fig. 3) to 3.5 pH derived samples. There are no additional peaks in XRD spectra for the entire experimental range.

The morphology of calcined samples (800 °C) was analyzed with JEOL JSM-7001F Field Emission Scanning Electron Microscope and the micrographs are compared in Fig. 4. The micrographs indicate clear morphological changes in the derived powders with respect to pH. The typical image of 3.5 pH derived powders shows bulged sphere like structure with sub-angular edges, primary particles were observed on the surface of the secondary particles. In pH 4.5, disk type particles were observed with sharp edges around the disk shape, thickness of the individual particles is high in the middle than at the edges. This disk shape particles are modified to rectangular shape of particles with size ranging from 100 to 500 nm in pH 5.5 synthesized powders and angular edges appear

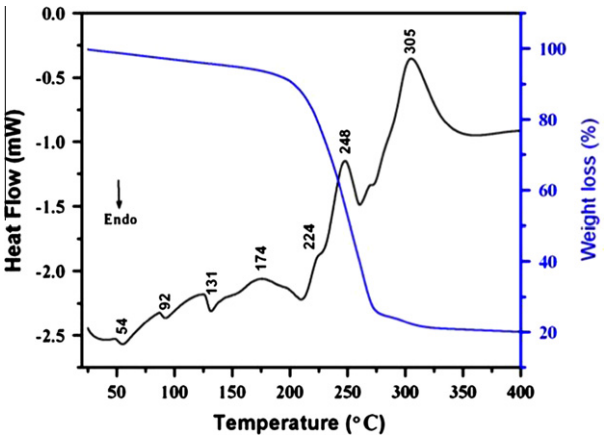

Fig. 1. TGA/DTA spectrum of synthesized gel pH 3.5.

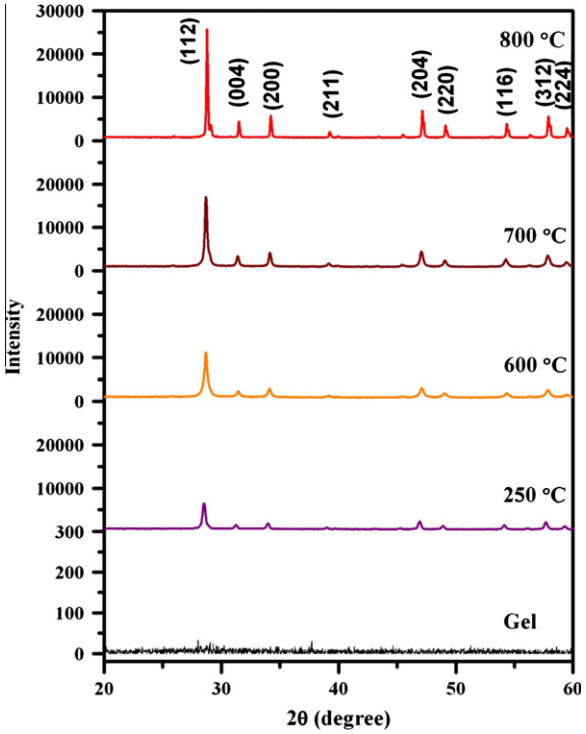

Fig. 2. Powder X-diffraction pattern for pH 3.5 NGW.

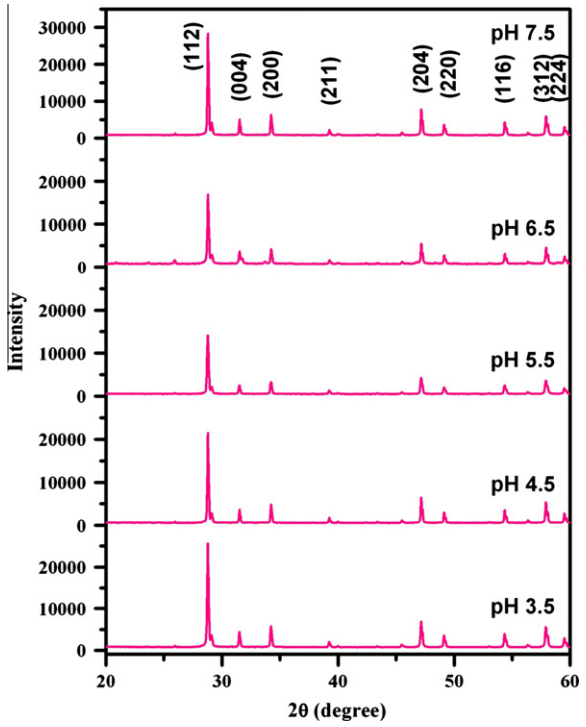

Fig. 3. Powder X-diffraction pattern for 800 °C calcined NGW.

on the surface. Double edged pyramid shape with angular edges was observed in 6.5 pH derived powders. Increasing the pH value to 7.5, the shape of the particles resembles the shape of 6.5 pH derived powders but with no sharp edges. The particles derived at 5.5, 6.5 and 7.5 pH lead to primary particles free of powders.

The FT-IR spectra for synthesized gels, pre-fired and high temperature calcined samples were recorded using Perkin–Elmer