

Low-agglomerated yttria nanopowders via decomposition of sulfate-doped precursor with transient morphology

R.P. Yavetskiy^{1,*}, D.Yu. Kosyanov¹, V.N. Baumer², A.G. Doroshenko¹, A.I. Fedorov², N.A. Matveevskaya¹, A.V. Tolmachev¹, O.M. Vovk¹

(1. Institute for Single Crystals of NAS of Ukraine, 60 Lenin Ave., Kharkov 61001, Ukraine; 2. State Scientific Institution "Institute for Single Crystals" of NAS of Ukraine, 60 Lenin Ave., Kharkov 61001, Ukraine)

Received 3 August 2013; revised 31 December 2013

Abstract: The fabrication peculiarities of low-agglomerated yttria (Y_2O_3) nanopowders via thermal decomposition of sulfate-doped precursor with transient morphology were studied. It was determined that $Y_2(OH)_5(NO_3)_x(CO_2)_y(SO_4)_z \cdot nH_2O$ ($n=1-2$) crystalline precursor underwent fragmentation and decomposition into isolated quasi-spherical Y_2O_3 particles upon calcination. Effect was connected with minimizing the free energy of the plate-like crystallites via reducing the contact surface until to the moment of spheroidization and attainment of isolation that occurred at $T=1100$ °C. Residual sulfate ions slowed down the surface diffusion during heat treatment thus retaining quasi-spherical morphology and low aggregation degree of Y_2O_3 nanopowders. Sulfate-doped yttria nanopowders with medium particle size of 53 ± 13 nm possessed improved sinterability in comparison with undoped ones arising from finer particle size, narrower particle distribution and lower agglomeration degree.

Keywords: precursor; transient morphology; sulfate-ions; yttria; nanopowders; particle size; sinterability; rare earths

Yttrium oxide is an important industrial material, which finds application in the production of refractories, in nuclear technologies, as a component of structural and functional ceramics and dopant material^[1]. Y_2O_3 nanopowders are used as nanophosphors for photonics and biomedicine, advanced laser, scintillation ceramics^[2,3], as well as a starting material for the preparation of laser ceramics based on yttrium aluminum garnet $Y_3Al_5O_{12}$ (YAG) by reactive sintering method^[4-7]. Typically, yttria nanopowders are obtained by chemical co-precipitation method with subsequent calcination of the precursor. Oxide nanopowders usually retain the precursor morphology, which results in formation of hard aggregates^[8]. Aggregation of nanopowder hinders full densification of ceramics to pore-free state due to differential sintering effect. This leads to degradation of the optical properties of ceramics because of the presence of residual pores which act as scattering centers. Among existing methods of obtaining low-agglomerated Y_2O_3 nanopowders (spray pyrolysis, Pechini sol-gel method, solvothermal and hydrothermal synthesis, laser vaporization of the target, etc. (see, for example, Refs. [9–13])), the chemical precipitation with subsequent calcination of the precursor has relatively high yield and does not require any sophisticated equipment, so is considered as one of the most prospective for synthesis of yttria nanopowders with the controlled parameters. Recently,

we have successfully obtained highly-transparent YAG:Nd ceramics by reactive sintering using home-made Y_2O_3 :Nd low-agglomerated monodisperse nanospheres and commercial alumina powders^[14]. This result clearly demonstrates that the agglomeration degree of yttrium oxide nanopowders is one of the key factors in the preparation of laser ceramic with garnet composition.

Recently, a new concept was proposed to prevent agglomeration of Y_2O_3 nanopowders via utilization of co-precipitated sulfate-doped precursors with transient morphology, which decompose upon calcination into low-agglomerated quasi-spherical particles^[15-18]. Breakdown of polycrystalline nano-rods or plates into isolated quasi-spherical particles during heat treatment is considered as a result of trend of every grain to minimize its total free energy by reducing the contact surface. Chemical precipitation of yttrium hydroxide with transient morphology is characterized by high productivity, large yield, and relatively high purity of final product^[17]. It has been reported that introduction of sulfate ions allows one to prevent agglomeration of yttria nanopowders^[10-17,19]. Moreover, sulfate-doped Y_2O_3 precursors may be beneficial to produce low-agglomerated highly-sinterable yttria nanopowders for obtaining of YAG laser ceramics by reactive sintering method^[6]. It should be noted that during synthesis of Y_2O_3 nanopowders for YAG laser ceramics, using a thermally-stable dispersing agent (e.g.,

Foundation item: Project supported by the National Academy of Sciences of Ukraine (78/13-H)

* **Corresponding author:** R.P. Yavetskiy (E-mail: yavetskiy@isc.kharkov.ua; Tel.: +38 0573410415)

DOI: 10.1016/S1002-0721(14)60074-0

silicon-containing) may lead to deviation from garnet stoichiometry (due to formation Si–O–Y chemical bonds^[20]). This leads to formation of impurity phases at grain boundaries and to degradation of optical properties of ceramics. When sulfate-containing additives are utilized for the synthesis of low-agglomerated oxide nanopowders this problem is not observed^[21–23]. Currently, the correlation between the doping of yttria precursor by sulfate ions and the agglomeration degree of resulting nanopowders has not been addressed in details. This work was devoted to study fabrication peculiarities of low-agglomerated yttria nanopowders as a component of YAG ceramics via decomposition of sulfate-doped precursor with transient morphology.

1 Experimental

Y₂O₃ nanocrystalline powders were obtained by chemical co-precipitation using ammonium hydroxide (NH₄OH, Sigma-Aldrich) as a precipitant followed by calcination of precursor. The 2 mol/L solution of NH₄OH was added to yttrium nitrate (0.25 mol/L) obtained by dissolving the commercial yttrium oxide (Y₂O₃ 99.999% (REO), REacton, Alfa-Aesar) in nitric acid (HNO₃, Sigma-Aldrich). The normal-strike co-precipitation route was performed at the molar ratio of reactants (R) NH₄OH/Y³⁺=4 and the temperature of 10 °C. The drip rate was about 3 mL/min. The introduction of SO₄²⁻ ions [SO₄²⁻]/[Y³⁺]=0–10 mol.%) was carried out after precipitation procedure by the addition of aqueous solution of ammonium sulfate ((NH₄)₂SO₄, Sigma-Aldrich). The obtained precipitate was aged for 3 h; vacuum filtrated and washed carefully with deionized water. After that the precursor was dried in air at temperature of 25 °C. Y₂O₃ nanopowders of different dispersion and morphology were obtained by the annealing of the precursor for 2 h in the temperature range of 600–1300 °C.

The morphology of precursor and Y₂O₃ nanopowders was investigated by a transmission electron microscopy (TEM) using an EM-125 (Selmi, Ukraine). A dilatometric analysis of products of calcination of the precursor was performed using a Netzsch 402 ED dilatometer. The heating rate was 10 °C/min, the alpha alumina was used as a reference. X-ray diffraction analysis (XRD) of the precursor and synthesized nanopowders was carried out using a SIEMENS D-500 X-ray diffractometer (graphite monochromator, Cu K α radiation) in the range of angles 2 θ =20°–80°. The PDF-1 JCPDS database of “EVA” search system included in the diffractometer software was used for identification of phases. The average size of crystallites was calculated by FullProf software using the powder diffractogram of LaB₆ for determination of the instrumental function of the line profile. The specific surface area of the powders was determined by Brunauer-Emmett-Teller method (BET). The average particle size

D_{BET} was calculated according to the equation: $D_{\text{BET}}=6/\rho \cdot S$ (where ρ is the material density (5.03 g/cm³ for Y₂O₃) and S is the specific surface area). The particle size distribution of synthesized nanopowders was measured using a Zetasizer 1000HSA (Malvern Instruments). The elemental composition of the nanopowders was detected by a CHNS-O elemental analyzer EA-3000; the detection limit is about 0.01 wt.% (EuroVector, Italy).

2 Results and discussion

As is known, precipitation of water solutions of yttrium nitrate with ammonium hydroxide in a weak alkaline medium leads to formation of the hydrated yttrium hydroxynitrates with RE₂(OH)_{6-x}(NO₃)_x·nH₂O general composition^[24,25]. According to differential thermal analysis data not presented in this work, the x value is close to 1 thus formed precursor has Y₂(OH)₅NO₃·nH₂O approximate composition. Crystal structure of this salt is formed by the positively charged metal-hydroxide Y(OH)₂⁺ layers and NO₃⁻ anions located in interlayer region. Sulfate ions added to the mother solution may interact with the precursor particles via physical adsorption mechanism and/or intercalation in the interlayer region. Replacement activity of interlayer NO₃⁻ ions by impurity anions of the mother solution is decreased as follows: CO₃²⁻>SO₄²⁻>OH>F>Cl>Br>NO₃⁻. Consequently, one can expect introduction of sulfate ions into crystal structure of the yttrium hydroxynitrate. This suggestion is confirmed by peculiarities of hydrated yttrium hydroxynitrate crystals structure, which has high isomorphic capacity for substitution in anion sublattice^[24,25]. Fig. 1 shows the sulfur content in sulfate-doped precursors of yttrium oxide depending on the [SO₄²⁻]/[Y³⁺] molar ratio. Sulfur was evaluated by chromatographic separation of gaseous combustion products in a dynamic atmosphere of oxygen. To determine upper limit of incorporation of SO₄²⁻ ions into Y₂(OH)₅NO₃·nH₂O structure addition of sulfate ions was performed in the [SO₄²⁻]/[Y³⁺]=0–10 mol.% range denoted below as S_X, where X corresponds to the quantity of introduced SO₄²⁻ ions during the syn-

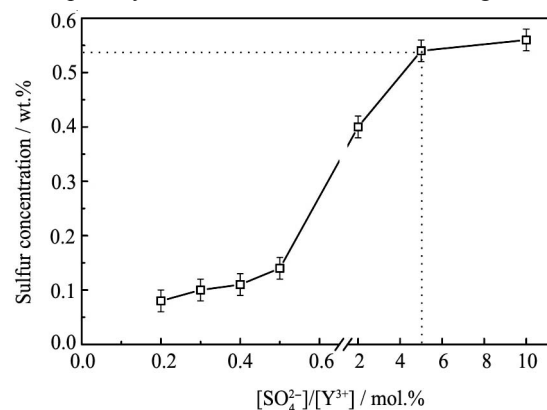


Fig. 1 Sulfur content in sulfate-doped precursors of yttrium oxide depending on the [SO₄²⁻]/[Y³⁺] molar ratio

Download English Version:

<https://daneshyari.com/en/article/1259393>

Download Persian Version:

<https://daneshyari.com/article/1259393>

[Daneshyari.com](https://daneshyari.com)