Synthesis of highly dispersed precursor nanopowders for $YAG:Yb$ ceramics by the use of hexamethylenetetramine

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Abstract. The effect of hexamethylenetetramine on the morphology, dispersion composition and chemical homogeneity of the $YAG:Yb$ ceramic nanopowders, obtained by the method of heterophase co-precipitation, followed by calcination (1100 °C) was studied. It was shown that the use of an aqueous hexamethylenetetramine solution allows obtaining $YAG:Yb$ nanopowders with the particles size of 40-70 nm with a degree of agglomeration of 2.54, which is significantly less than that in comparison with the powders, obtained by precipitation in ammonia.

1. Introduction

Ceramics based on ytrrium-aluminum garnet, in particular, $YAG:Yb$ is one of the promising materials for the optics and solid-state lasers manufacture. Such ceramics should have high transparency and high density. These properties substantially depend on the characteristics of the initial precursor powder: its purity, morphology, and dispersion. The problem of obtaining the monodisperse precursor powder with the required morphology while maintaining the purity and homogeneity of the chemical composition is of great importance in modern materials science in the field of ceramics.

The most commonly used precipitants are an aqueous urea solution, solutions of ammonium bicarbonates and carbonates, and an aqueous ammonia solution [1-5]. Hexamethylenetetramine (hexamine) is a promising precipitant, but the process of precipitation when use hexamine as a precipitant are not well understood. In this regard, the aim of this work was to conduct a comparative analysis of the properties of the precursor powders and $YAG:Yb$ ceramic powders obtained via precipitation by aqueous solutions of ammonia and hexamine.

2. Materials and Methods

In this work, for the synthesis of powders of $YAG:Yb$ composition, we used a concentrated aqueous ammonia solution and a hexamine solution (1.25 M). The choice of hexamine concentration is based on the results of previous studies [3]. Samples were synthesized by reverse heterophase coprecipitation by spraying a salts solution into an alkaline precipitant solution. The obtained precursors (samples A1 and H1) were dried in air and then ball-milled using the wet method in a Pulverizette 5 planetary mill under the same conditions.
Ceramic powders (samples A2 and H2) were synthesized by high-temperature treatment of A1 and H1 precursor powders in the air at a temperature of 1100 °C in an LHT 08/18 chamber furnace. The morphology of the obtained samples was studied using a MIRA3-LMH scanning electron microscope. The specific surface area was measured using a 3Flex specific surface area and porosity analyzer. To study the particle size distribution, an Analysette 22 MicroTec laser particle size analyzer was used. The phase composition of the samples was determined using an ARL Xtra, ThermoScientific X-ray diffractometer. The calculation of the average size of the agglomerates in powders was performed by the following equation:

\[
D_{\text{BET}} = \frac{6}{\rho \times S_{\text{BET}}},
\]

where \( \rho \) – density of YAG: Yb, g/cm³, \( S_{\text{BET}} \) – specific surface area, m²/g.

The size of nanocrystallites was determined using the Scherrer formula:

\[
D_{\text{XRD}} = \frac{0.89 \times \lambda}{\beta \times \cos \Theta},
\]

where \( \lambda \) – CuKα radiation wavelength (0.15406 nm), \( \beta \) – width at half maximum of the diffraction peak.

3. Results and Discussion

The results of X-ray diffraction analysis showed that in both samples, after the precipitation A1 and H1 powders were amorphous, as evidenced by the absence of X-ray reflections in the diffraction patterns. After heat treatment, samples A2 and H2 consisted of a 100% garnet phase.

Studies have shown that the morphology of samples synthesized using ammonia (A1, A2) and hexamine (H1, H2) was significantly different. As follows from the scanning electron microscopy results (Fig. 1), when using ammonia, denser A1 powder was formed, as compared to H1 sample synthesized using hexamine. After high-temperature treatment, fundamental differences in the samples were retained. Ceramic powder A2 had a denser microstructure than H2 sample, which was characterized by much less agglomeration of particles (Fig. 1).

**Figure 1.** SEM micrographs of the samples:
A1 and H1 – precursor powders; A2 and H2 – ceramic powders
In A2 ceramic powder, obtained from A1 precursor powder “neck bridges” between the particles were formed during the high-temperature processing. As a result, A2 ceramic powder consisted of rigid agglomerates ranging in size from 0.78 to 5.80 µm.

In the case of the use of hexamine as the precipitant, H2 powder had a smoothed surface topography of the particles and a narrower size distribution (Tab. 1). Differences in morphology and particle size distribution reflected in differences in the specific surface area of the samples. Ceramic powder H2 had a higher specific surface area (13.39 m²/g) than A2 powder (7.50 m²/g).

Analysis of A2 ceramic powder showed that it formed by agglomerates, which size significantly exceeds the average size of crystallites (Tab. 1). Therefore, a high degree of agglomeration (69.17) of these powders is consequential. In H2 sample obtained using hexamine, the number of primary crystallites in the agglomerate is much lower and reaches a value of 2.54.

| Name of sample | Precipitant                                      | Particle size distribution | Specific surface area (SBET), m²/g | The crystallite size (D_XRD), nm | The degree of agglomeration (n) |
|----------------|--------------------------------------------------|----------------------------|-----------------------------------|----------------------------------|--------------------------------|
| A1             | Concentrated ammonia solution                     | 1.27 4.26 13.92            | 51.57                             |                                  |                                |
| H1             | Aqueous hexamine solution (1,25 M)                | 1.09 3.62 11.41            | 65.72                             |                                  |                                |
| A2             | Concentrated ammonia solution                     | 0.78 1.95 5.80             | 7.50                              | 41.00                            | 69.17                          |
| H2             | Aqueous hexamine solution (1,25 M)                | 0.17 0.89 2.91             | 13.39                             | 69.03                            | 2.54                           |

4. Conclusion

According to the results of the study, it was concluded that the use of hexamine allows one to obtain a low agglomerated, highly dispersed powder with a homogeneous chemical and phase composition. This powder characterized by good formability and low-temperature sintering of ceramic compacts, which is an important condition for reducing porosity and improving the optical properties of ceramics. Therefore, it can be argued that hexamine is a promising precipitant for the synthesis of YAG:Yb ceramic powders.

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