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# Synthesis of yttrium aluminum garnet nanoparticles in confined environment, and their characterization

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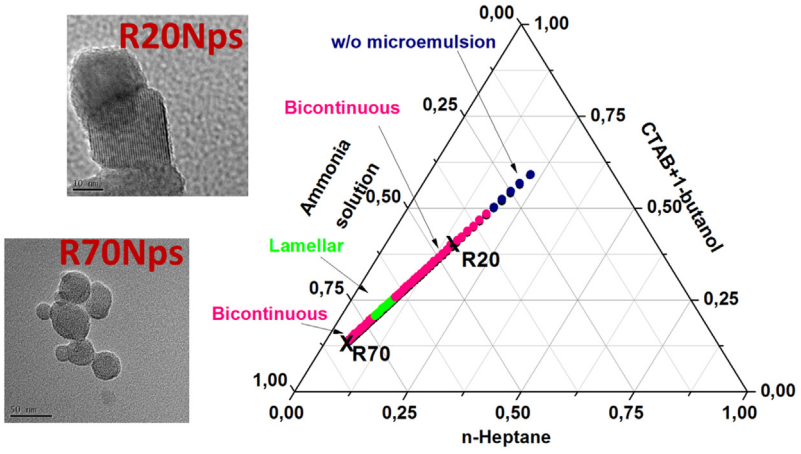
## HIGHLIGHTS

- A correlation between structure of microemulsion and morphology and structure of YAG nanopowder is evidenced.
- A structural model for SAXS data analysis is proposed.
- The microemulsion phase behavior depends on the aqueous phase content.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Nanopowders of *yttrium aluminum garnet* (YAG, $Y_3Al_5O_{12}$) have been prepared by thermal treatment of hydroxides obtained by synthesis in a confined environment constituted by water/Cetyltrimethylammonium bromide (CTAB)/1-butanol/n-heptane.

The phase behavior of the above system has been investigated on varying the water/CTAB molar ratio (R) at constant 1-butanol/CTAB and heptane/CTAB molar ratio. The dispersed aqueous phases were constituted by solutions of ammonia and of yttrium and aluminum nitrates, respectively. Measures of Kinematic Viscosity, Electrical Conductivity and Small Angle X-ray Scattering have been carried out. It was found that, on increasing the ammonia solution content the system evolves from a water in oil microemulsion to a bicontinuous one to a lamellar system and then it return to be bicontinuous, the yttrium and aluminum nitrate solution stabilizes the bicontinuous phase preventing the formation of the lamellar phase.

The precursor synthesis was performed by mixing two microemulsions containing reactants at the same R, 20 and 70, respectively. The YAG nanopowders obtained from precursor calcination have been characterized by means of Wide Angle X-ray Scattering and Transmission Electron Microscopy.

*Abbreviations:* NH3, ammonia solution; NO3, nitrates solution.

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The obtained nanopowders were constituted by nanoparticles showing strong differences in terms of size and aggregation that depend on the microemulsion structure.



## 1. Introduction

Yttrium Aluminum Garnet (YAG, $Y_3Al_5O_{12}$), with a cubic structure in the space group Ia-3d, doped with lanthanides ions, has received a great deal of attention because of its interesting technological applications such inorganic electroluminescence displays, X-ray scintillators, lasers, and white light LED [1]. In general, the optical properties of nanocrystals are expected to be dependent on the doping agent, on the particle size and its distribution and on morphology that may be influenced by the synthesis route [2–4]. As a consequence, several chemical routes such as co-precitation [5,6], sol-gel [7,8], Pechini method [9], solvo-thermal synthesis [10] and others have been used. All methods involve post-synthesis treatments at high temperature necessary to obtain the garnet phase avoiding the formation of secondary phases. The thermal treatment induces the formation of big agglomerated particles.

The synthesis in confined environment like a microemulsion gave better results, in term of shorter heating time, small particle size and narrow particle size distribution [11]. Furman et al. obtained Ce:YAG nanoparticles having specific optical properties by an emulsion route [12]. Jun at al. successfully prepared Nd:YAG nanoparticles with weak agglomeration and diameters of 40 and 80 nm using a novel approach called co-microemulsion–microwave heating [10]. Some of us prepared YAG nanopowders, constituted by small crystalline nanoparticles showing a low tendency to agglomerate, in a water/CTAB/1-butanol/n-heptane microemulsion [13].

The ability of surfactants to self-assemble into well-defined structures has constituted one of the main advantages for the design and synthesis of several inorganic materials with nano-sized dimensions. The structures formed by self-assembly of the surfactant have been used as template for the synthesis of nano- and *meso*-porous materials [14–16] and the accuracy and reproducibility of the self-assembly structures process has been seen as a way of achieving control of materials architecture at the nanometer scale. As a consequence, the number of papers dealing with surfactant-templated synthesis of inorganic materials has dramatically increased in the recent years [17–19]. This approach to nanomaterials preparation has triggered substantial interest both in the surface chemistry and the materials chemistry community. In particular, an effect of reaction media has been observed on particles size control in CdS and mixed oxides nanoparticles synthesis [20,21].

Among the different type of surfactant supramolecular structures, microemulsions play a very important role in nanofabrication [22].

The term microemulsion, in its most general use, denotes an oil/water mixture thermodynamically stabilized by, at least, a third component usually a surfactant able to reduce the water-oil interfacial tension. Over the past decades, it has been shown that microemulsion can assume a variety of microstructures. These comprise phases consisting of droplets of oil-in-water (o/w microemulsions or $L_1$ phases), or water-in-oil droplets (w/o microemulsions or $L_2$ phases) as well as bicontinuous phases. The microstructure mainly depends on the organization of the surfactant rich film that separates oil and water domains.

In a previous work, microemulsions were successfully used to obtain a YAG nanopowder constituted by small crystalline nanoparticles showing a low tendency to agglomerate [13]. On the account of close relationship between the structure of the reaction system and the shape and size of the nanoparticles synthesized [21], we decided to investigate the phase behavior of reactants aqueous solution/CTAB/butanol/n-heptane quaternary microemulsions with different R values where the dispersed phase is an ammonia and yttrium and aluminum nitrate solution, respectively. The relationship between the structure of the microemulsion and the properties of the YAG nanopowders obtained by thermal treatment of the hydroxides produced in this reaction medium has been investigated for two R-values.

The ability to characterize and control the structure of a microemulsion used in nanofabrication is of the uttermost importance in order to obtain a final product with the desired properties.

Small Angle Scattering (SAS) gives detailed information about the supramolecular organization in nano-dispersed system [23]. The number of structural models proposed for the analysis of scattering data is very high [24] and, usually, the choice among them depends on the knowledge of physical properties of the system. In particular, X-rays Small Angle Scattering (SAXS) has been used to investigate the phase behavior of the microemulsion.

Furthermore, kinematic viscosity, and electrical conductivity measurements were used to obtain useful information on the microemulsion properties.

Transmission Electron Microscopy (TEM) and Wide Angle X-rays Scattering (WAXS) were used to characterize the YAG powders obtained.

## 2. Materials and methods

### 2.1. Materials

Cetyltrimethylammonium bromide (CTAB) (Aldrich ≥98%), 1-butanol (Aldrich, 99.8%), n-heptane (Sigma-Aldrich, 99%), deionized water, $Y(NO_3)_3{\cdot}6H_2O$ (Sigma-Aldrich, 99.8%), $Al(NO_3)_3{\cdot}9H_2O$ (Sigma-Aldrich, 99.8%) and ammonia solution (Sigma-Aldrich 28%) were used as received. The conductance of deionized water was < 1.5 $\mu S\,m^{-1}$.

### 2.2. Microemulsion preparation

The microemulsion composition is described by three parameters, P, R, S defined as:

$$P = \frac{mol_{1-butanol}}{mol_{CTAB}}; R = \frac{mol_{water}}{mol_{CTAB}}; S = \frac{mol_{n-heptane}}{mol_{CTAB}} \quad (1)$$

The microemulsions were obtained by weighting the appropriate amount of *n*-heptane (the continuous oil phase), aqueous solution (the dispersed phase), CTAB (the surfactant) and 1-butanol (the cosurfactant). P and S were fixed at 4.1 and 13.3, respectively. R varied from 4.3 to 70.0 (the minimum and the maximum solution amount that grants for a homogeneous system, respectively).

The yttrium and aluminum nitrate solution (30 and 50 mmol $L^{-1}$, respectively) was prepared by dissolving $Y(NO_3)_3{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ in water. The microemulsions containing the aqueous solution of nitrates were prepared by using appropriate amounts of the above solution. The microemulsions containing the ammonia solution were prepared by fixing