



# Preparation and characterization of nanodispersions of yttria, yttrium aluminium garnet and lutetium aluminium garnet

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## ABSTRACT

Refractory and chemically inert nanoparticulate solids like yttria, yttrium aluminium garnet or lutetium aluminium garnet are notoriously difficult to disperse in aqueous solution, although such dispersions might prove useful for 2D- and 3D-printing, deposition of films or other shaping procedures for ceramic green bodies. This work reports on experiments to prepare such dispersions from nanopowders, using a range of selected carboxylic acids as ligands for electrostatic charging and stabilization of the various nanomaterials. The assessment of the system properties achieved combines  $\zeta$ -potential and viscosity (flow curve) measurements in the resulting colloidal systems. Calculations of the molecular electrostatic potential of the ligands were used to correlate the molecular structure of the ligands and their capability to dock to the surface of the solid particles. The colloid chemical data received have then been interpreted on this background; citric acid and polyacrylic acid have been identified as the most attractive dispersants.

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## 1. Introduction

Nanopowders of yttria ( $Y_2O_3$ ), yttrium aluminium garnet ( $Y_3Al_5O_{12}$ , YAG) and lutetium aluminium garnet ( $Lu_3Al_5O_{12}$ , LuAG) can be prepared by various methods [1–3], among others through precipitation in glycols (so-called solvothermal or glycolthermal synthesis) [4].

The special interest in these nanopowders comes from the fact, that they are excellent hosts for lanthanide-doped optical materials, e.g. solid state lasers. In comparison to micron-sized powders, reduced sintering temperatures can be achieved with nanopowders, which is an important aspect when developing synthetic procedures for transparent ceramics. Moreover, nanopowders are necessary, when colloidal formulations for printing, electrophoretic deposition, plasma spraying or similar techniques have to be developed. However, aqueous dispersions of the above mentioned materials have seldomly been investigated in depth, although the properties in the dispersed state will be crucial for the final properties of the ceramics or films prepared from them. As an example, the colloidal state of co-dispersions of alumina and yttria (as characterized by flow curves and  $\zeta$ -potential) determines the properties of YAG ceramics after sintering [5]. More recent work investigated YAG:Nd dispersions, but only as a function of sulfate content, and not in a systematic fashion [6].

For colloidal stability, either entropic stabilization by adsorbed macromolecules or suited methods of electrostatic particle charging are needed; polyelectrolytes may bring in both effects. Inter-

pretation of the stability achieved conventionally uses the  $\zeta$ -potential (characterizing the adsorption of ions) and the thickness of the double layer (characterized by Debye's length  $r_D$ ); both parameters are defined in the framework of DLVO theory [7]. This model has been extended to cases at higher ionic strengths, since a double layer with non-vanishing  $\zeta$ -potential can be formed also by ion segregation effects in the water layer attached to the particle surfaces [8]. As a rule of thumb, a nanodispersion stabilized solely by electrostatic repulsion is considered to be metastable, when the absolute value of its  $\zeta$ -potential is larger than ca. 30 mV.

Metastability of a nanocolloidal system means, that in principle unavoidable aggregation and growth processes are slowed down extremely. The main reason for this behaviour, besides a high electrostatic energy barrier between the particles, is the fact, that in nanodispersions the diffuse layer around a nanoparticle may be larger than the particle itself [9]. This is the case here, since in order to prepare dispersions with low sedimentation tendency, suited for techniques like printing or electrophoretic deposition, the particle size needs to be well below 100 nm [10] and thus falls into this range.

For many colloids based on metal oxides, changing the pH value from low to high values shifts the  $\zeta$ -potential from positive to negative values, due to effects of protonation and deprotonation of OH-groups at the surface of the colloidal particles [11]; in some cases this kind of charging is already sufficient for stabilization. In cases, where the pH-range necessary for sufficient charging is inconvenient for chemical or technical reasons, specific adsorption of other ions than  $H^+$  or  $OH^-$  might be useful, provided they prove to be capable to adjust the range of metastability to the pH-region needed. For obvious practical reasons, metastability should be guaranteed for a pH-range as broad as possible.

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Once particles are prepared and exposed to the right medium, tailored milling processes may need to be applied for deagglomeration, if possible exerting predominantly shearing forces on the particle aggregates (“colloid milling” in a specially designed ball mill). The absence of compressive forces avoids excessive damage to the particles during milling; this is an important aspect especially when optical properties of the particles (e.g. absorption and fluorescence) are concerned.

Since all materials investigated in this work are oxides, the surface chemistry in aqueous environment will be dominated by OH-groups; adsorption of ligands therefore in all cases most probably will take place through polar interaction with these entities. Natural choice for ligands under these conditions are polar molecules like carboxylic acids or alcohols. In order to avoid excessive amounts of foreign materials short-chain hydroxy acids have been selected (lactic acid, malonic acid, citric acid and  $\iota(+)$ -tartaric acid), complemented with polyacrylic acid as an example for a polyelectrolyte; the molecular structure of its repeating unit is very similar to the smaller molecules under investigation. The acids were selected in such a manner, that (due to the number and location of polar groups available and their ability to act cooperatively) different adsorption characteristics on the particle surface can be expected (see Table 1 with definition of acronyms used, based on data from [12]).

To compare the effects, nanoparticulate alumina ( $\text{Al}_2\text{O}_3$ ) dispersions were used and characterized in this work as a control and bench mark, since the colloid-chemical behaviour of this material is very well documented [13–16].

## 2. Experimental

Commercially available nanopowders of  $\text{Al}_2\text{O}_3$  (Sigma Aldrich) and  $\text{Y}_2\text{O}_3$  (Alfa Aesar) with very high purity were used without further modification.

YAG and LuAG nanopowders were synthesized in an autoclave using a glycothermal method with yttrium acetate or lutetium acetate as precursor materials, respectively. 10 mmol of aluminium triisopropylate were mixed in a glass reaction vessel with stoichiometric amounts of yttrium acetate or lutetium acetate. 40 ml 1,4-butanediol were added to this mixture under stirring. The reaction vessel was placed in an autoclave (Parr Instruments;  $V = 0.5$  l). After purging with nitrogen, the autoclave was locked and heated up at a rate of 2.3 K/min to 300 °C. This temperature was held for 2 h via Parr Instruments 4843 controller. After cooling down to room temperature over night, the samples were washed three times with ethanol. The ethanol was separated from the particles by centrifugation. Drying of the samples was carried out at 80 °C for 2 h in a drying chamber [17].

**Table 1**  
Carboxylic acids and polyelectrolyte used in the experiments; data taken from [12].

Compound	Acidity, $pK_a$	Structure
Lactic acid LA	$pK_a = 3.86$	$\text{CH}_3\text{-CHOH-COOH}$
Malonic acid MA	$pK_{a1} = 2.83$ ; $pK_{a2} = 5.69$	$\text{HOOC-CH}_2\text{-COOH}$
Tartaric acid TA	$pK_{a1} = 2.99$ ; $pK_{a2} = 4.40$	$\text{HOOC-CHOH-CHOH-COOH}$
Citric acid CA	$pK_{a1} = 3.09$ ; $pK_{a2} = 4.75$ ; $pK_{a3} = 5.41$	$\begin{array}{c} \text{COOH} \\   \\ \text{HOOC-CH}_2\text{-C-CH}_2\text{-COOH} \\   \\ \text{OH} \end{array}$
Polyacrylic acid PAA	$pK_a = 6.0$	$\left( \begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{---C---C---} \\   \quad   \\ \text{H} \quad \text{COOH} \end{array} \right)_n$

The crystal structure was verified by powder X-ray diffraction (XRD) (Rigaku MiniFlex II), using Cu  $K\alpha_1$  radiation, with an increment of  $\Delta(2\theta) = 0.028$ .

Morphological and chemical analysis were performed with a Zeiss-LEO 982 “Gemini” scanning electron microscope (SEM), equipped with a field effect electron source and a Bruker-Nano (xflash 5030) energy dispersive X-ray (EDX) analytical system.

For the preparation of dispersions, 10 wt.% of nanomaterials was dispersed in water by ultrasonication and magnetic stirring for 15 min, to break coarse agglomerates. Subsequently, colloid milling (*Pulverisette 7 premium line*, Fritsch Planetary Micro Mill) with zirconia balls (100 g of balls with 0.5 mm diameter) in a 80 ml zirconia grinding bowl (Fritsch) was performed (capacity for dispersion to be treated was 10 ml). Standard procedures recommended for colloid milling were used (6 cycles of 5 min with a pause of 30 min). Speed was individually optimized for each material: 900 rpm, 1000 rpm and 200 rpm for yttria, YAG and LuAG, respectively. The pH of the mixtures was set by addition of various carboxylic acids, polyacrylic acid and their sodium salts, if necessary.

$\iota(+)$ -tartaric acid/sodium tartrate (TA/ST), lactic acid/sodium lactate (LA/SL), malonic acid/sodium malonate (MA/SM) and citric acid/sodium citrate (CA/SC) were purchased from Sigma Aldrich and used as delivered. Polyacrylic acid/ sodium polyacrylate (PAA/PSA) of molecular weight of 240.000 were purchased from Alfa Aesar and used without modification.

Particle size measurements (using dynamic light scattering, DLS) and  $\zeta$ -potential measurements on the dispersions obtained were performed using a ZetaSizer Nano Z system from Malvern Instruments, together with a standard pH meter (SevenMulti, Mettler Toledo). Curves of  $\zeta$ -potential over pH were recorded by first adding the free carboxylic acid to the dispersion to decrease the pH-value to the acidic range, and then by titration with the conjugated sodium salt solution to increase the pH-value to the alkaline range. All pH-adjusters were used in a concentration of 1–2 mol/l. By adding volumes of ca. 0.005 ml, the pH-value typically changed by one unit. From repeated measurements on calibration samples, the uncertainty of an individual  $\zeta$ -potential reading was estimated to be ca.  $\pm 3$  mV.

Flow curve measurements were performed at room temperature (23 °C, controlled), on dispersions with absolute  $\zeta$ -potential higher than 20 mV, using a rotational viscometer (Thermo Scientific HAAKE Viscotester 550) with a double gap sensor head (NV) for low-viscosity fluids. Suspensions were measured directly after preparation, without waiting times, to avoid potential problems with sedimentation. A full sweep of the shear rate from 0 to 1000  $\text{s}^{-1}$  to record the flow curve took 240 s.

Calculations of charge distributions on the ligand molecules were performed using the GAMESS-US package [18], for visualization purposes MacMolPlt was used [19]. For the smaller ligands,

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