

Synthesis and structural characterization of YVO_3 prepared by sol–gel acrylamide polymerization and solid state reaction methods

G. Herrera · E. Chavira · J. Jimenez-Mier · L. Baños · J. Guzmán · C. Flores

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Abstract The formation of the YVO_3 compound obtained by sol–gel acrylamide polymerization is reported. This synthesis method is contrasted with solid state reaction. Differential thermal analysis (DTA) results show the formation of YVO_3 at 805 °C compared with 1312 °C for solid state reaction. Thermogravimetric analysis (TG) results show that between 400 and 600 °C the denaturalization of the organic part, ethylenediamine, and the decomposition of nitrates occur. The evolution of YVO_4 into YVO_3 was also studied by X-ray powder diffraction (XRD). The refinement results obtained for both YVO_3 samples show an orthorhombic phase with Pbnm (62) space group and lattice parameters: $a = 5.283 \text{ \AA}$, $b = 5.605 \text{ \AA}$ and $c = 7.580 \text{ \AA}$. Grain size and morphology evolution for different heat treatments were studied with scanning electron microscopy (SEM). The use of sol–gel acrylamide synthesis allows us to start with a homogeneous grain distribution with a mean size of $5.03 \pm 0.65 \text{ nm}$ growing up to $4.11 \pm 0.87 \text{ \mu m}$ in YVO_4 . After reduction to YVO_3 the final grain size was $2.87 \pm 0.10 \text{ \mu m}$ also with

grain size homogeneity. This is in contrast with samples prepared by solid state reaction for which the grain size starts (YVO_4) between 1 and 7.0 \mu m and ends (YVO_3) with a size distribution centered at $90.32 \pm 74.46 \text{ \mu m}$. Transmission electron microscopy (TEM) results corroborate XRD results. Energy dispersive X-ray (EDX) results are in agreement with theoretical values.

Keywords Ceramics · Crystal growth · Electron microscopy (TEM, SEM) · Nanomaterials

1 Introduction

Electronic properties of transition metal oxide compounds with strong electron–electron correlations have attracted attention since the advent of high-Tc superconductors. Recently, the perovskite YVO_3 has been studied intensively as an example of a Mott transition system. It is of the great importance to clarify the physical properties of the Mott–Hubbard insulator YVO_3 compound for which the spin, charge and orbital ordering are still unexplained, with a lack of consensus on their microscopic origin [1–9].

The YVO_3 compound presents the perovskite structure of GdFeO_3 with an orthorhombic phase, Pbnm space group and well determined unit cell parameters [10–14]. Due to the distorted perovskite structure this compound exhibits interesting physical properties and wide range of possibilities for practical applications in electronic devices.

The research into electronic properties of this compound requires very pure materials in order to optimize its particular properties. The most commonly used method is solid state reaction. However, this method has clear disadvantages. For example, uncontrolled crystalline growth occurs, ending in grain-size non-uniformity. For YVO_3

G. Herrera (✉)

Posgrado en Ciencias Químicas, Universidad Nacional Autónoma de México, AP 70-360, 04510 Mexico D.F., Mexico
e-mail: guillermo.herrera@nucleares.unam.mx

E. Chavira · L. Baños · J. Guzmán · C. Flores
Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, AP 70-360, 04510 Mexico D.F., Mexico

J. Jimenez-Mier
Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, AP 70-360, 04510 Mexico D.F., Mexico

Present Address:

J. Guzmán
CICATA-LEGARIA-IPN, Calz. Legaria # 694, Col. Irrigación, c.p.11500 Mexico D.F., Mexico

compound the literature reports a synthesis temperature $>1000\text{ }^{\circ}\text{C}$ [15]. On the other hand, wet chemistry and particularly sol–gel processing is one of the most promising way to get an excellent homogenization at an atomic scale of the elements and a high reactivity of the precursor. The procedure for obtaining the acrylamide gels was developed by Sin and Odier [16–18]. In 1989 the first paper related to this novel route by Douy and Odier appeared [19]. Later Douy extended this work to scale up the process for industrial practice [20], and also began the study of the use of acrylamide network using chelated cation solutions to prepare oxide precursors [21]. Recently this method was used to control the homogeneity and therefore improve thermoelectric properties of samples [22].

In this regard YVO_4 compound has already been successfully prepared by this method [23]. The main purpose of this work is to obtain YVO_3 using YVO_4 compounds prepared by sol–gel acrylamide polymerization in order to obtain particles in the range of nanoscale. We also compare the resulting grain morphology with samples prepared by solid state reaction. In the work reported here, we found that the homogeneity of the grain size in the YVO_4 precursor prepared by acrylamide is maintained at the end of synthesis.

2 Experimental procedure

2.1 Synthesis of sol–gel acrylamide

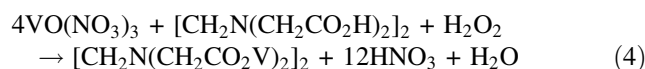
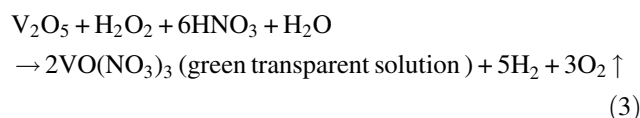
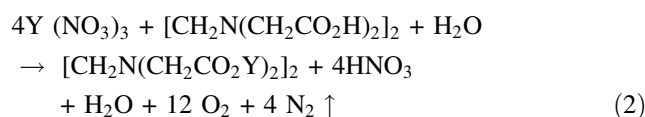
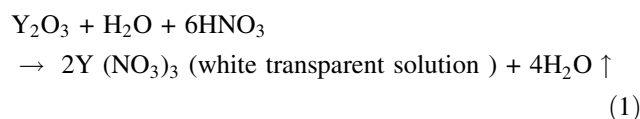
2.1.1 Sol formation

High purity Y_2O_3 (ALDRICH, 99.99%) and V_2O_5 (CE-RAC, 99.9%) were used in the synthesis of the yttrium vanadate by sol–gel acrylamide polymerization. A 50 wt % stoichiometric proportion of Y_2O_3 was dissolved completely in 150 mL of distilled water with 7–10 mL of HNO_3 (J.T. Baker 69–70%) to obtained a transparent solution of $2\text{Y}(\text{NO}_3)_3$ and 50 wt % of V_2O_5 was dissolved in H_2O_2 (this agent was used to increase the reaction speed) with 3–5 mL of HNO_3 at last to obtain 2 g of the sample. The resulting solution was mixed under continuous magnetic stirring at $90\text{ }^{\circ}\text{C}$ ($\pm 0.05\text{ }^{\circ}\text{C}$) in an Ika CERAMAG Midi, in order to increase the velocity and the homogeneity of the solution.

2.1.2 Gel formation

Each transparent solution was mixed with the amount related in weight percentage of each cation of the chelating agent, ethylenediaminetetraacetic acid (EDTA, $[\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2]_2$ Fluka 99%) using the molar ratio 1:1. A lower concentration of EDTA would allow Y and V to

react with acrylamide monomers, forming complexes and thus impeding the gel formation. A higher concentration of EDTA would only cause the precipitation of EDTA in the solution before one gets the gel. The mixture was kept at $80\text{--}90\text{ }^{\circ}\text{C}$ with constant stirring. We used this chelating agent to encapsulate the rare earth element Y (+3) and the transition element V (+5) metals ions. This step is designed to prevent the ions from forming complexes until the in situ reactions start. The ions then keep their stability during the decomposition of EDTA. The reactions for each cation in this step are:



After this step the pH value was 0.83. The solution was then mixed, with 10–20 mL of NH_4OH (J.T. Baker 28–30%) in order to adjust the pH to 3.8 because the fast acrylamide polymerization proceeds generally in aqueous medium whose pH is close to neutral [16]. This process was performed at room temperature.

To this solution (300 mL) we added a 10 wt % considering the final solution volume of acrylamide ($\text{H}_2\text{C} = \text{CHCONH}_2$ (Fluka 99.9%)) monomers to start the polymerization [16] and to accelerate the gel formation. We also added 1 wt % of the cross-linker N,N'-methylenebisacrylamide ($\text{C}_7\text{H}_{10}\text{N}_2\text{O}_2$ (Fluka 99.5%)). Also 1 wt % of α,α' -azoisobutyramidine dihydrochloride (AIBN, $\text{C}_8\text{H}_{18}\text{N}_6 \cdot 2\text{HCl}$ (Fluka 98%)) is added to regulate the weight of acrylamide and to increase the velocity of interconnections. The thermopolymerization process was carried out under continuous magnetic stirring at $80\text{ }^{\circ}\text{C}$ until an opaque green viscous gel is produced. The gel is obtained by heating to $90\text{ }^{\circ}\text{C}$ for 8 min.

2.1.3 Xerogel formation

The gel obtained was dried at $100\text{ }^{\circ}\text{C}$ for 12 h to eliminate water in a Felisa oven ($\pm 4\text{ }^{\circ}\text{C}$). The temperature was then raised to $200\text{ }^{\circ}\text{C}$, resulting in a porous foam material called xerogel. This xerogel was grinded in an agate RM 100 mortar grinder (Retsch), and the powder was heated first at

250 °C. Next we increased the temperature in 100 °C steps up to 800 °C. In this stage an important organic phase and amorphous materials are removed and nanocrystals are grown. To go from one step to the next the temperature was increased at a rate of 5 °C/min.

At the end of the synthesis we obtained 94.5% (1.89 g) of the sample. The mixture was then compacted into pellets (diameter 13 mm thickness $1.0\text{--}1.5 \pm 0.05$ mm) exerting a pressure of 4 ton/cm² in a Osyma Press for 45 min in vacuum and it was subjected to thermal treatment at 800 °C for 4 days and 1 hour in air. Finally, we decreased the temperature to 30 °C with rate of 10 °C/min.

2.2 Solid state reaction

Polycrystalline yttrium vanadate was prepared by solid state reaction. In this technique, raw materials Y₂O₃, (ALDRICH, 99.99 %) and V₂O₅ (CERAC, 99.9 %) were weighted, mixed with ethanol (J. T. Baker 70%) and milled during 15 min in an agate mortar to form a slurry. The milled powder was heated at 800 °C in a thermolyne 46100 furnace (± 4 °C) during one day in air.

The resulting material was compressed into pellets (diameter 13 mm thickness $1.0\text{--}1.5 \pm 0.05$ mm) exerting a pressure of 4 ton/cm² in a Osyma Press for 15 min in vacuum. Compacted specimens at the beginning were sintered at 1200 °C during four days in air. Then we decreased the temperature up to 800 °C at a rate of 10 °C/min. This is the initial temperature to start the heat treatments that were used to increase the grain size and is the same that was used for the sol–gel acrylamide samples.

3 Characterization techniques

In order to determine the temperature interval in which the reaction should be carried out differential thermal analysis (DTA) and thermogravimetric analysis (TG) measurements were performed using Modulated DSC 9210, TA instruments. The nanocrystals and amorphous material of xerogel (sol–gel acrylamide) and polycrystals prepared by solid state reaction were placed in platinum crucibles and heated starting at room temperature and up to 1400 °C. The heating rates were of 10 °C/min in air to obtain DTA spectra. DTA was used to evaluate the thermal decomposition of the samples prepared by both sol–gel acrylamide and solid state reaction. TG spectra were obtained up to 1000 °C with heating rates of 10 °C/min in air in order to follow the thermal transformations such as decomposition, phase transformation, polymorphism, melting point, degradation temperatures, purity, chemical stability, volatilization of organic material, etc. of samples. Then we only obtained DTA spectra for powders with YVO₄

compound prepared by both synthesis methods to follow the transformation of YVO₄ into YVO₃ compounds. These DTA results were obtained up to 1400 °C with heating rates of 10 °C/min in a N₂ atmosphere. Crystalline phases were identified by X-ray powder diffraction (XRD), using a Bruker–AXS D8–Advance diffractometer with λ (CuK _{α}) = 1.54 Å radiation. This equipment is able to detect up to a minimum of 1% of impurities. Diffraction patterns were collected at room temperature over the 2θ range 5°–70° with a step size of 0.010° and time per step of 0.6 s. The refinement was made by powdercell software [23] on a XRD pattern collected at room temperature between 20° and 120° with a step size of 0.020° and time per step of 9 s. The sample was grinded in order to avoid the influence of easy directions.

The change in morphology of YVO₃ obtained by different heat treatments was investigated by scanning electron microscopy (SEM) on a Cambridge-Leica Stereoscan 400. The micrographs between 2.5 and 20.00 kX, were taken with a voltage of 20 kV, current intensity of 1000 pA and WD = 25 mm. The Energy Dispersive X-Ray (EDX) was performed on the same equipment, with an Oxford/Link System electron probe microanalyser (EPMA).

The crystal structure of the YVO₃ compound was studied by transmission electron microscopy (TEM) with a JEM—1200EXII Jeol microscope. The diffraction patterns were taken with a voltage of 120 kV and a current intensity of 70–80 μ A, with camera length 100 cm. The specimens were prepared by dispersing small amounts of the YVO₃ nanocrystals in toluene (SIGMA-ALDRICH, 99.8%).

4 Results and discussion

4.1 Differential thermal analysis

To make a comparison of the thermal changes that occurred during synthesis of the samples prepared by sol–gel with respect to the samples prepared by solid state 13.300 mg of the amorphous xerogel and 7.900 mg of the polycrystalline powder were analyzed by DTA. The DTA results for the sample prepared by sol–gel acrylamide polymerization show three different regions see Fig. 1(a). The first one is the region between 25 and 200 °C. It indicates the evaporation of water with an endothermic peak at 98 °C, the endothermic peak due to the evaporation of H₂O₂ at 160 °C, and the initial denaturalization of the organic part. The second region between 200 °C and 590 °C shows two peaks. The first one corresponds to an exothermic reaction of the NO_x group with residuals of the organic part at 248 °C, that is in agreement with Fernández et al. [24], and an endothermal process at

approximately 300 °C probably due an important volatilization of the organic part. The second one is an exothermal peaks centered between 514 and 565 °C where the decomposition of ethylenediamine, the denaturalization of organic part and the intermolecular evaporation of nitrates is achieved. The final region between 590 and 1400 °C corresponds to the phase transition from the amorphous xerogel to the formation of a nanocrystalline YVO_4 compound at 600 °C with the complete decomposition of carbon compound because if the reaction temperature decreases also maybe the reduction reaction begins at low temperature. These results were corroborated by XRD. They are in agreement with the TG analysis for the compound prepared by sol–gel acrylamide that shows an important loss of the organic part in the interval between 300 and 600 °C. At 800 °C one observes the evaporation of an important part of nitrates and the decomposition of a considerable part of the organic part see Fig. 1(b). The TG spectrum for the compound prepared by solid state reaction is different because it has no organic part. A possible explanation for this lower nanocrystallization phase in the sample prepared by sol–gel acrylamide is due to the fact that the synthesis method provides a mixing of elements at a molecular level and it also reduces the diffusion path, accelerates the crystallization process until one obtains a stable YVO_4 compound. The results shown in Fig. 1(c) give significant differences between temperatures that allow us to fix the initial conditions of heat treatments. One can observe in the DTA spectra that the transformation of YVO_4 compound to YVO_3 compound for sol–gel

acrylamide occurs at 804.5 °C compared to solid state reaction that presents the transformation at 1312 °C. These results would indicate that 800 °C is a useful temperature to start the crystal growth in the YVO_4 compound. However, for reasons that will become clear later, we chose to do it at 850 °C.

4.2 X-ray powder diffraction

Figure 2 illustrates the XRD pattern evolution from the nanocrystalline phase into the YVO_4 crystalline phase prepared by sol–gel acrylamide polymerization. Fig. 2(a) shows a XRD pattern of milled powders of xerogel at 300 °C. This temperature was maintained during 12 h. The pattern demonstrates some reflections related to the initial formation of the YVO_4 compound. However not all reflections are present in this pattern, indicating that the desired crystalline structure is not present at this stage. Also, one can observe in the width of the peaks, the broadening shown is related to a smaller particle size. Using the Debye–Scherrer relationship with peak position 25.140 (200) and an interplanar distance 0.353948 it was possible to determine a particle size of 3.5 nm, in agreement with the TEM results given in Sect. 3.6.

Figure 2(b) shows the XRD pattern obtained at 550 °C. One can see how the formation of the YVO_4 compound starts to define better these reflections as expected from DTA results. The reflections here are narrower indicating larger crystallites.

Fig. 1 (a) DTA results show transition from the amorphous xerogel (100 °C) to the formation of a nanocrystalline YVO_4 compound at 600 °C. TGA results (b) corroborate the evaporation of water and H_2O_2 ; between 25 and 200 °C, the decomposition of ethylenediamine and the initial evaporation of nitrates between 200 and 590 °C and the evaporation of an important part of nitrates at 700 °C. DTA (c) show the transition of YVO_4 compound into YVO_3 compound at 804 °C in sol–gel acrylamide instead of 1312 °C for solid state reaction; both results were obtained in a N_2 atmosphere

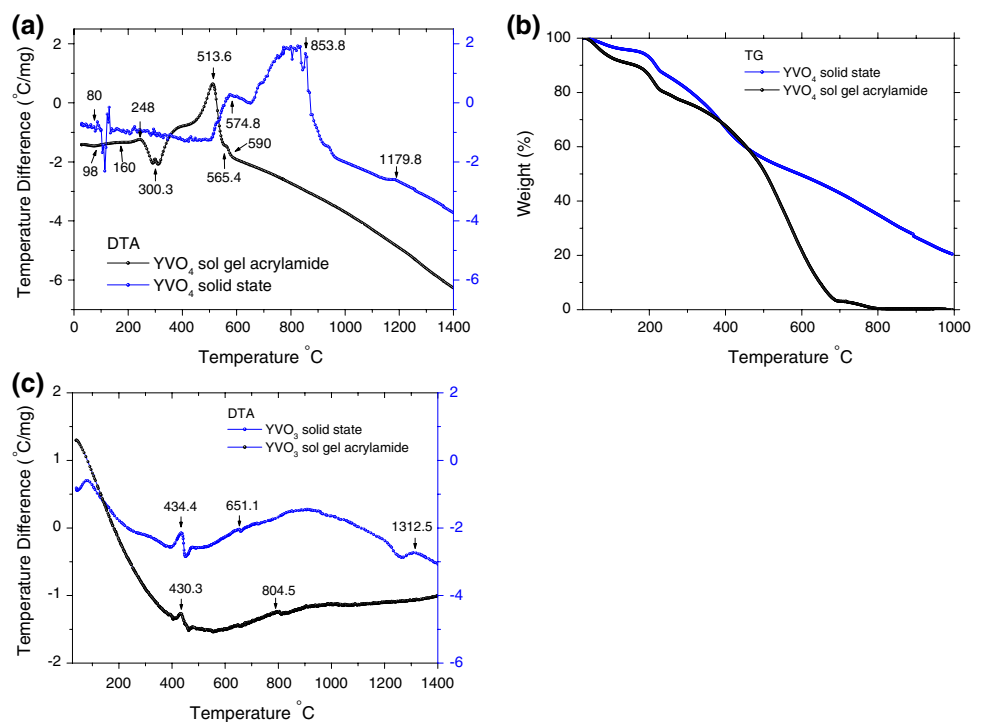


Fig. 2 XRD pattern evolution of YVO_4 compound. (a)–(c) correspond to samples prepared by sol–gel acrylamide polymerization. (a) crystalline phase of xerogel powders at 300 °C. (b) YVO_4 crystal formation starts to define better these reflections at 550 °C. (c) XRD results at 800 °C with all reflections. (left). (d) XRD pattern of YVO_4 compound prepared by solid state reaction obtained after the heat treatment at 1200 °C during four days in air(right)

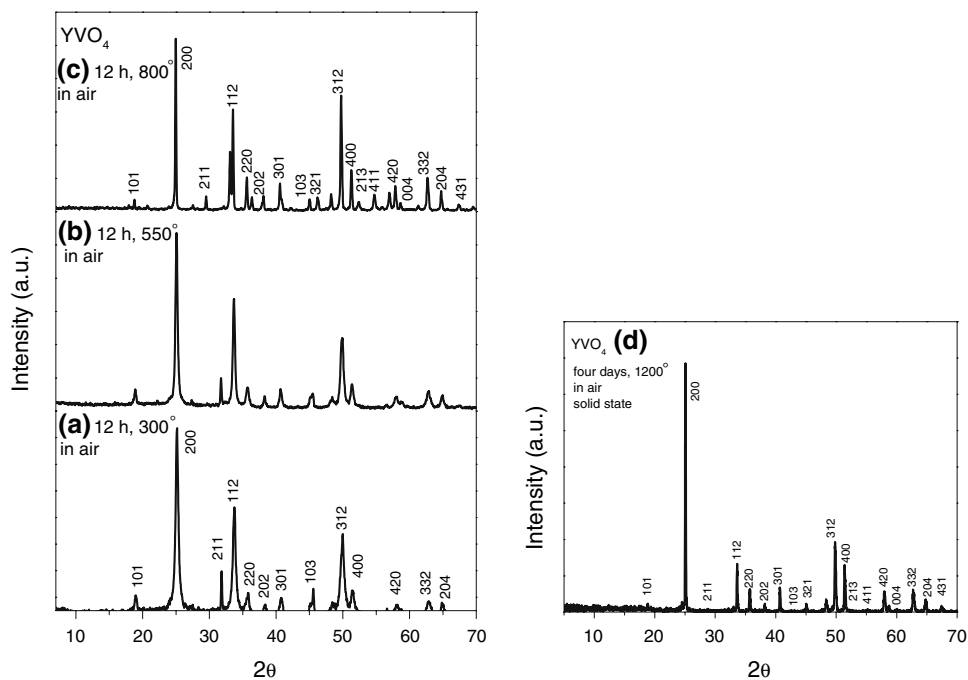


Figure 2(c) shows the XRD pattern of the powders kept at 800 °C during 12 h. This pattern is similar to the one obtained for powders kept at 600 °C during 12 h, with all reflections related to YVO_4 compound. The single phase pattern shows reflections related to the YVO_4 (PDF 72-0274) crystal phase for both powders prepared by sol–gel acrylamide and solid state reaction (Fig. 2d). In both cases the observation of only YVO_4 compound leads us to conclude that the coordination number for Y is 3+ and for V is 5+.

A refinement of YVO_4 compound with powder XRD data gives a tetragonal unit cell with a space group $I4_1/amd$ (141). The resulting lattice parameters are: $a = b = 7.1212 \text{ \AA}$ and $c = 6.2908 \text{ \AA}$, $R_p = 0.0462$, $R_{wp} = 0.0393$ and $R_{exp} = 0.367$. These results are in agreement with the values reported in the literature [25–28]. XRD effects at 800 °C suggest this to be the optimal temperature to start the crystal growth. DTA curve of Fig. 1(c) synthesized by sol–gel acrylamide polymerization we observe an exothermic alteration that in addition could be related to an amorphous–crystal transformations. Unfortunately we did not register the cooling curve. These examinations were corroborated by scanning electron microscopy.

Once we obtained a stable YVO_4 compound, the temperature was increased in 10 °C steps up to 870 °C. In each step the temperature was kept constant for three weeks in air. These heat treatments were made for the samples prepared by both sol–gel acrylamide and solid state reaction in order to increase the particle size as can be seen in the FWHM of reflections taken during these heat treatments.

To obtain YVO_3 compound, the single phase YVO_4 compound powders prepared by both synthesis methods were compacted into pellets and then reduced with a metallic Zr rod (ALDRICH 99%). Both the sample and Zr were enclosed in a quartz tube in vacuum. The temperature was kept at 850 °C during 27 days. After this period of time the sample was quenched in ice, in this step one can observe the oxidation of Zr. This metal was used as a gatherer in order to obtain the desired crystalline phase YVO_3 compound.

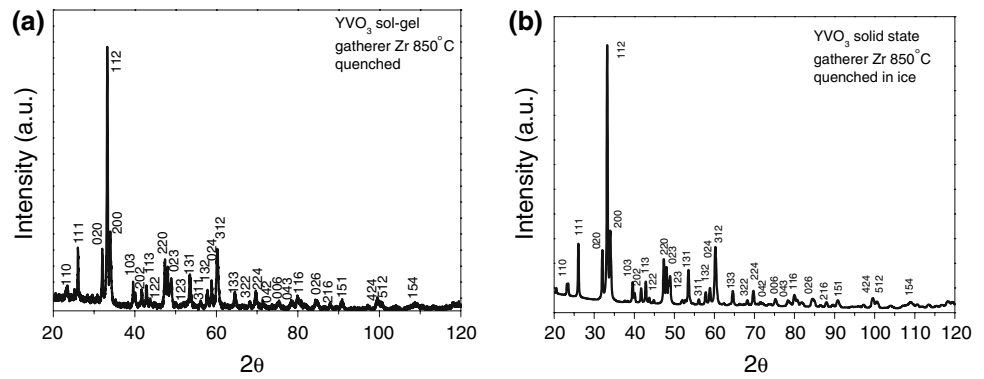
Figure 3 shows the XRD patterns of YVO_3 compound (PDF 25-1066) at room temperature, (a) gives the results for the sample prepared by sol–gel acrylamide and (b) for the sample prepared by solid state reaction. The YVO_3 compound has an orthorhombic phase with space group $Pbnm$ (62). The lattice parameters were: $a = 5.2839 \text{ \AA}$, $b = 5.6055 \text{ \AA}$ and $c = 7.5800 \text{ \AA}$. Statistical factors of $R_p = 0.01462$, $R_{wp} = 0.01938$, and $R_{exp} = 0.67339$ were obtained for sol–gel acrylamide. The statistical factors of $R_p = 0.01156$, $R_{wp} = 0.01513$, and $R_{exp} = 0.6700$ were obtained for solid state reaction.

4.3 Scanning electron microscopy

4.3.1 Sol–gel acrylamide

To continue with the study of YVO_4 we are interested to investigate the relationship between the grain size and the temperature. Then with these results we will study the evolution of the grain size distribution of samples prepared for both synthesis methods. Grain size and morphology of

Fig. 3 (a) XRD pattern of YVO_3 compound prepared by sol-gel acrylamide; (b) XRD pattern of sample prepared by solid state reaction; both samples were, reduced with metallic Zr. The refinement was determined by powdercell [29]



the sample prepared by both synthesis methods were studied by Carnoy 2.0 version software [30]. The grain size distributions curves allow a determination of the grain size average D_m and its root mean square dispersion s using the software Origin 6.0 [31].

We start this analysis with the sample prepared by sol-gel acrylamide polymerization. Figure 4 shows the micrograph of YVO_4 compound powders at the end of synthesis at 800 °C during 12 h in air. This micrograph was taken at 20.0 kX to better define the grain size at a nanoscale level. It can be seen that the grain size is very small and homogeneous respect to the sample prepared by solid state reaction presented below. In fact its average is 5.03 ± 0.65 nm. The resolution of this image is not very good due to the fact that these powders were charging because this sample is an insulator. In order to avoid this charging a thin gold layer was spread on the surface of powders during three seconds with the help of a sputter coater. Also, the powders were kept in contact with the aluminum crucible using silver paint layer (SPI Supplies).

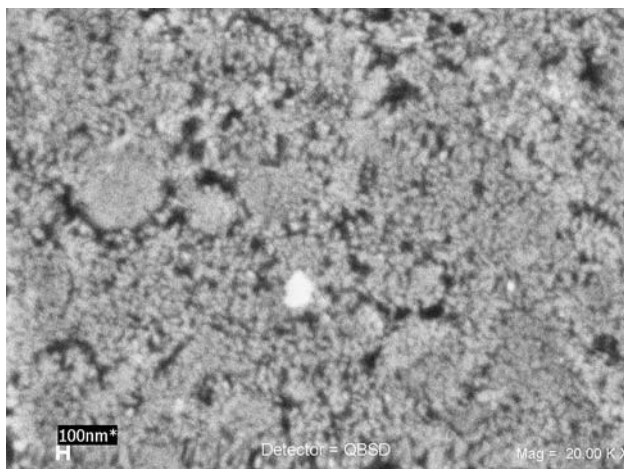


Fig. 4 SEM micrograph of surface of YVO_4 compound at the end of synthesis at 800 °C during 12 h in air, prepared by sol-gel acrylamide, with $D_m = 5.03 \pm 0.65$ nm

Figure 5 shows the micrograph of the pellet surface of the YVO_4 compound prepared by sol-gel and kept at 800 °C during 4 days and 1 h in air. One can observe a gradual increase of grain size due to the initial agglomeration of nanoparticles to form bigger grains that result from the heat treatment at high temperature. This agglomeration presents less homogeneous grain size distribution. In this case the grain size average was 2.21 ± 0.10 μm . The micrograph was taken at 5.00 kX respect to the last one because this is the magnification for which one can see the grain morphology in more detail.

Figure 6 shows the micrograph of YVO_4 compound at 860 °C. In order to transform the small particles into dense crystals, the sample was kept during four weeks in air. This micrograph reveals that with this heat treatment we obtained two different grain size distributions. The grain size averages are 3.58 ± 3.27 μm and 7.75 ± 1.49 μm . In the top right corner of this micrograph one can see that the crystal starts to grow. The porosity present in some of the grains indicates that the time spent at this temperature was not enough to accomplish volume diffusion successfully.

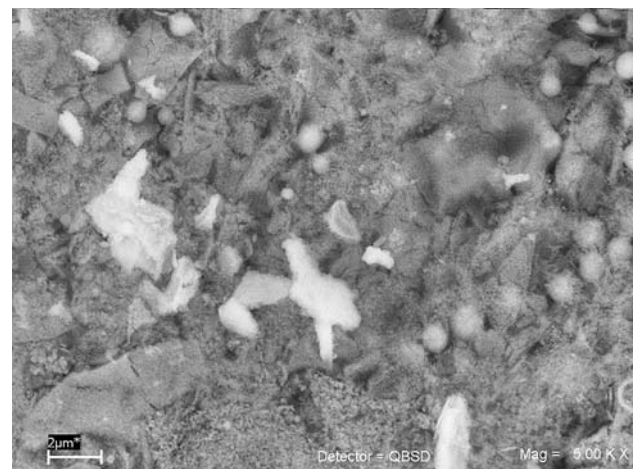


Fig. 5 SEM micrograph on surface of YVO_4 compound at 800 °C during 4 days and 1 h, $D_m = 2.21 \pm 0.10$ μm

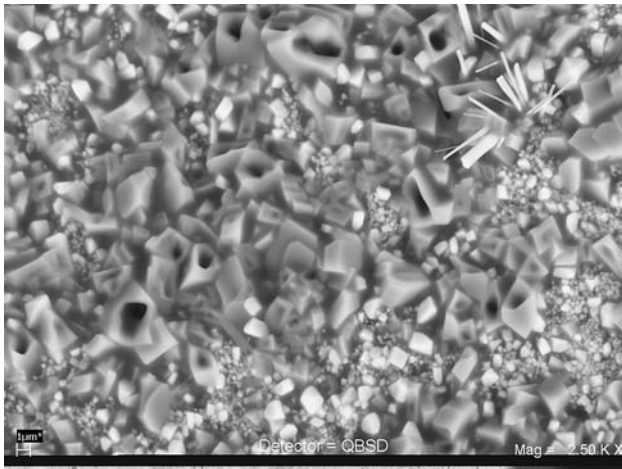


Fig. 6 SEM micrograph on surface of YVO₄ compound at 860 °C. The grain size shown a bimodal distribution with D_m equal to $3.58 \pm 3.27 \mu\text{m}$ and $7.75 \pm 1.49 \mu\text{m}$

Figure 7 shows a micrograph of YVO₄ compound with other heat treatment at 870 °C. The temperature was kept constant during three weeks with the idea of closing down the pores generated in the previous heat treatment. The pores effectively disappeared with this heat treatment. Then we found the conditions to increase the density in the pellet grains. The probable mechanism involved in this treatment is the reduction of the surface energy. This micrograph was taken before the reduction of YVO₄ compound into YVO₃ compound and one can see more defined grains. The grain size is more homogeneous. The grain size distribution gives an average size of $4.11 \pm 0.87 \mu\text{m}$. The surface of the pellet shows a rough surface and one can see the single crystals with the help of the optical microscope. Our SEM results are in agreement with the XRD results.

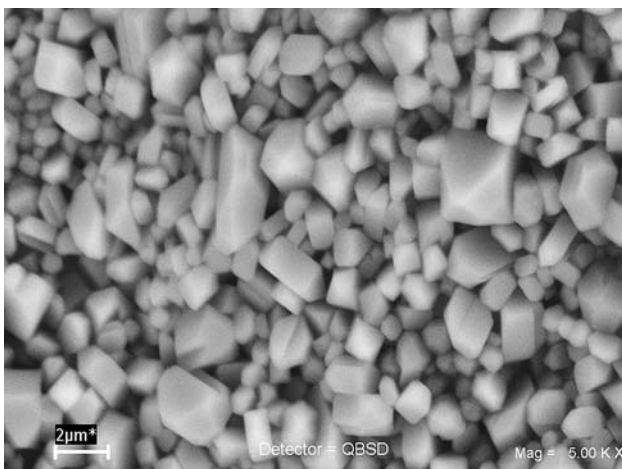


Fig. 7 SEM micrograph on surface of YVO₄ compound at 870 °C, in this stage the grain size is more homogeneous and the grain size distribution gives $D_m = 4.11 \pm 0.87 \mu\text{m}$



Fig. 8 SEM micrograph on surface of YVO₃ compound at 850 °C, one can observe how grain size decreases with an average around $2.87 \pm 0.10 \mu\text{m}$, and at the same time the distribution is homogeneous

Figure 8 shows YVO₃ compound micrograph on the surface pellet, one can observe a homogenous grain size distribution with regular shape as a result of the heat treatment kept at 850 °C during 1 month using a metallic Zr as gatherer. The grain size decreases to an average around $2.87 \pm 0.10 \mu\text{m}$. It was observed that the grain size decreases with the increase in the temperature of the heat treatments. This result is in agreement with XRD pattern. The surface and bulk color of the sample transformed from white (YVO₄ compound) to metallic gray (YVO₃ compound). In this step one can corroborate the oxygen reduction from O₄ to O₃. The temperature was kept at 850 °C because at high temperatures (855–890 °C) grain size starts to increase without order due to the semi-fusion between grains. For that reason, the optimum temperature to increase the grain size is 850 °C.

Figure 9 shows the evolution of crystal growth at different heat treatments for samples prepared by sol-gel acrylamide. The temperature was kept at 850 °C. The period of time varies from three weeks up to four weeks. One can see a decrease in the grain size and an improvement in the grain size homogeneity at the end of the heat treatments. Using to the law $D = G(t - \tau)$ where G is the crystal growth speed [32] we obtained $G = 4.0 \text{ nm/day}$ for the sample prepared by sol-gel acrylamide.

4.3.2 Solid state reaction

As one can expect for this synthesis method there is a big difference between the morphology at the end of final reaction temperature (microns) respect to the sol-gel acrylamide route. The observed morphology presented in Fig. 10 shows considerable variations in sizes and grain

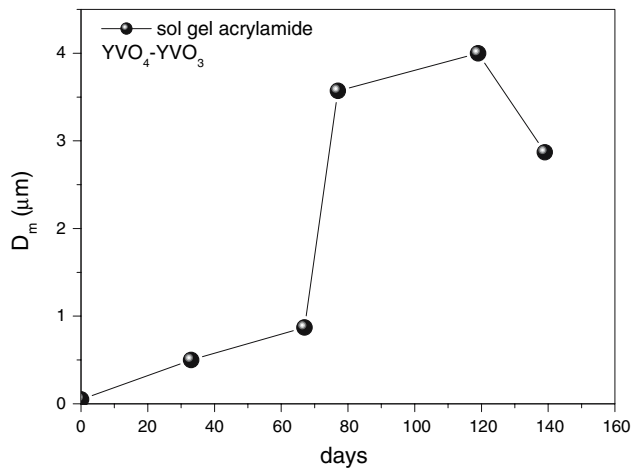


Fig. 9 Graph of the evolution of grain size versus the time of different heat treatments for the sample prepared by sol-gel acrylamide

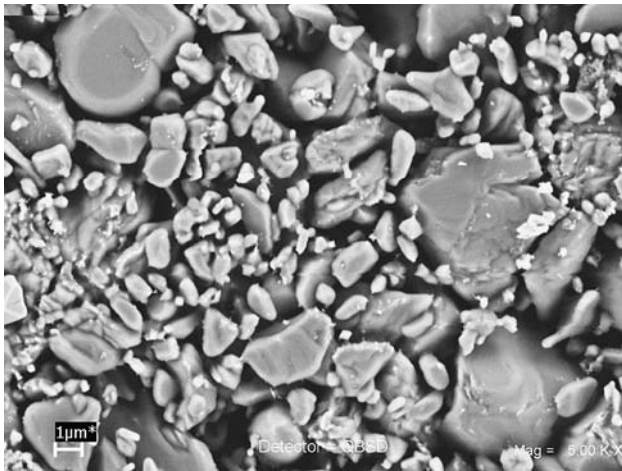


Fig. 10 SEM micrograph of surface of YVO_3 compound pellet prepared by solid state reaction at $1200\text{ }^\circ\text{C}$ during four days in air. Three D_m were determined: $2.13 \pm 0.72\ \mu\text{m}$; $3.43 \pm 0.59\ \mu\text{m}$; $5.83 \pm 1.24\ \mu\text{m}$

shapes. The micrograph was taken at 5.0 kX on the surface pellet of the YVO_4 sample. We chose this magnification to better define the grains on a larger scale. The sample was heated to $1200\text{ }^\circ\text{C}$ during four days in air in order to obtain the YVO_4 compound. In contrast to the sample prepared by sol-gel acrylamide, this micrograph reveals that for the solid state sample the grain sizes are less homogeneous in shape and size and vary between 1 and $7\ \mu\text{m}$.

In the sol-gel acrylamide case, the higher specific surface decrease due to the lower temperature, therefore it is more favorable to release the stored grain boundary energy compared to the sample prepared by solid state reaction [33]. As one can see in the DTA results all reagents in the sol-gel sample react at lower temperature. This is clear in the initial formation of YVO_4 at $400\text{ }^\circ\text{C}$ with the

production of a grain size distribution with high shape and size homogeneity in comparison with the solid state reaction that presents several exothermic peaks. In the later case all reagents start to react at higher temperatures ($830\text{--}850\text{ }^\circ\text{C}$) to initiate the formation of YVO_4 with the consequence of a non-homogenous grain size distribution.

Figure 11 shows the micrograph of YVO_3 compound obtained by solid state reaction and maintained at $850\text{ }^\circ\text{C}$ during one month in air using a metallic Zr as gatherer. This heat treatment was chosen in order to keep the same temperature and time conditions of crystal growth for both synthesis methods. One can observe that time was not sufficient to improve the crystal growth as can be seen on the micrograph. The final grain size was $90.32 \pm 74.46\ \mu\text{m}$, also, one can observe the non-homogeneity in the grain size distribution. These SEM results for both solid state and sol-gel samples indicate that the optimum formation of high-purity fine grain size YVO_3 compound is $850\text{ }^\circ\text{C}$. We found that higher temperatures will cause crystallite melting.

The DTA in Fig. 1(c) gives information about differences in the transformation of YVO_4 to YVO_3 that can be related to differences in the grain morphology. In the sol-gel sample this transformation is finished at $800\text{ }^\circ\text{C}$ while for the solid state sample this occurs in the interval between 650 and $1320\text{ }^\circ\text{C}$. A reduction in the grain size of the sol-gel sample occurs at the end of the transformation. Nothing similar is found for the solid state sample, where one finds a gradual increase in the grain size even after production of YVO_3 is finished.

Figure 12 shows the evolution of crystal growth at different heat treatments for samples prepared by solid state reaction. The temperature was kept at $850\text{ }^\circ\text{C}$ during four months. This period of time is the same that was used

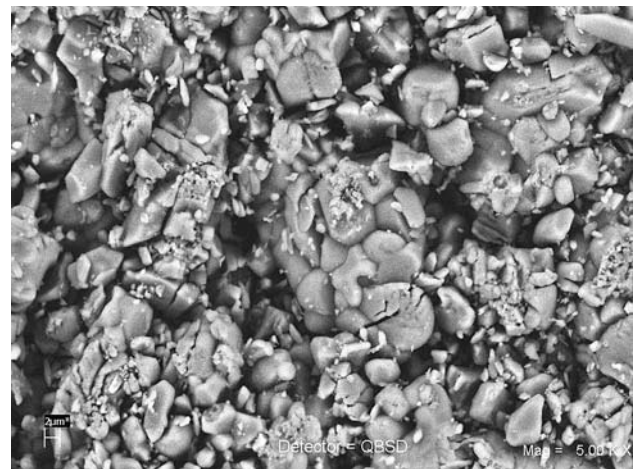


Fig. 11 SEM micrograph of surface of YVO_3 compound into a pellet topology at $850\text{ }^\circ\text{C}$, prepared by solid state reaction, $D_m = 90.32 \pm 74.46\ \mu\text{m}$

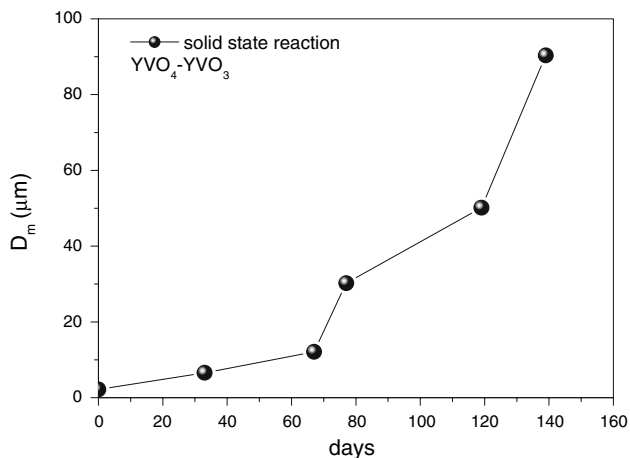


Fig. 12 Graph of the evolution of grain size versus the time of different heat treatments for the sample prepared by solid state reaction

for the samples prepared by sol–gel. In this graph one can see that the kinetics of crystal growth is faster compared to the crystal growth in samples prepared by sol–gel acrylamide. We obtain $G = 0.7 \mu\text{m}/\text{day}$.

The grain boundary of the sol–gel acrylamide sample presents a high mobility and thus shows a rapid grain growth up to 120 days (Fig. 9). At this stage almost all pores disappear, as can be seen in Fig. 7. The reduction of the sample to obtain YVO_3 compound seems to stop this migration of the grain boundaries. A possible explanation for this effect is that the stored energy of the grain boundary was not enough to provide the driving force to continue the crystal growth [34]. In the sample prepared by solid state reaction even after 120 days the minimization of grain boundary energy continues (Fig. 12). This may be due to boundary migration of larger grains (Fig. 11).

4.4 Energy dispersive X-ray

Global EDX results are presented in Fig. 13. The spectra show peaks related to the elements involved in the synthesis method. These spectra were taken on the surface of a

pellet in the final YVO_3 compound at 850°C during 1 month. The percentage concentrations of cations Y and V in the YVO_3 compound determined by this technique are in agreement with that obtained by stoichiometry analysis. This behaviour was observed for both samples.

4.5 Transmission electron microscopy

The YVO_3 fine powders (nanocrystals) prepared by sol–gel acrylamide polymerization were observed by TEM. The Electron diffraction pattern of YVO_3 compound particle is shown in Fig. 14(a) sol–gel acrylamide (b) solid state reaction; and it was indexed as the [200] zone axis with an orthorhombic Bravais lattice. The particle size by sol–gel acrylamide is 3.9 nm. This is in agreement with the XRD results. The obtained lattice parameters were approximately $a = 5.281 \text{ \AA}$, $b = 5.623 \text{ \AA}$ and $c = 7.605 \text{ \AA}$ with a c/a ratio about 1.44. The angle between [111] and [202] zone axes is 47° , close to the measured angle between [202] and [111]. There is a little difference with respect to lattice parameters determined by XRD. One possible explanation for this discrepancy is that TEM diffraction is a local technique while XRD takes into account an average on the sample.

5 Conclusions

We compared the formation of YVO_3 compound by reduction of YVO_4 compound produced by solid state reaction and by sol–gel acrylamide polymerization. The crystal structure of both precursor and final product were determined by X-ray powder diffraction and by transmission electron microscopy. We found a significant decrease in the formation temperature for YVO_4 compound prepared by sol–gel acrylamide at 600°C compared with the solid state reaction sample at 1200°C . The temperature of 850°C for reduction and therefore formation of the YVO_3 compound is, however, the same for both procedures. The grain size distribution of the sol–gel acrylamide produced

Fig. 13 Global energy dispersive X-ray pattern on surface of YVO_3 compound prepared by sol–gel acrylamide polymerization (left). EDS for YVO_3 compound prepared by solid state reaction (right)

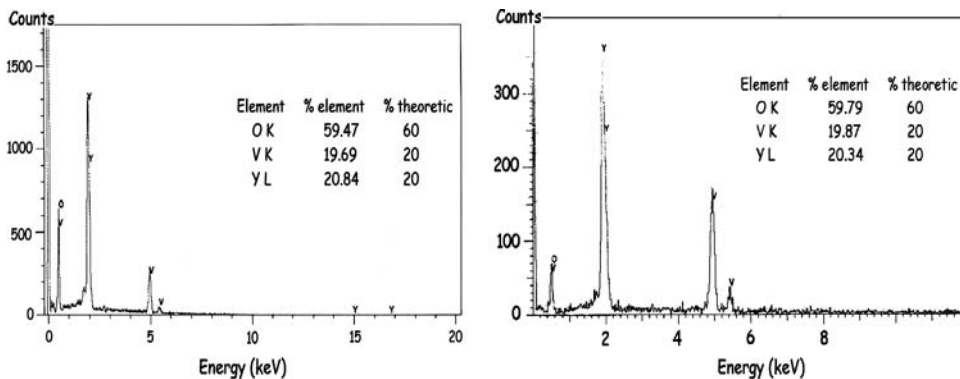
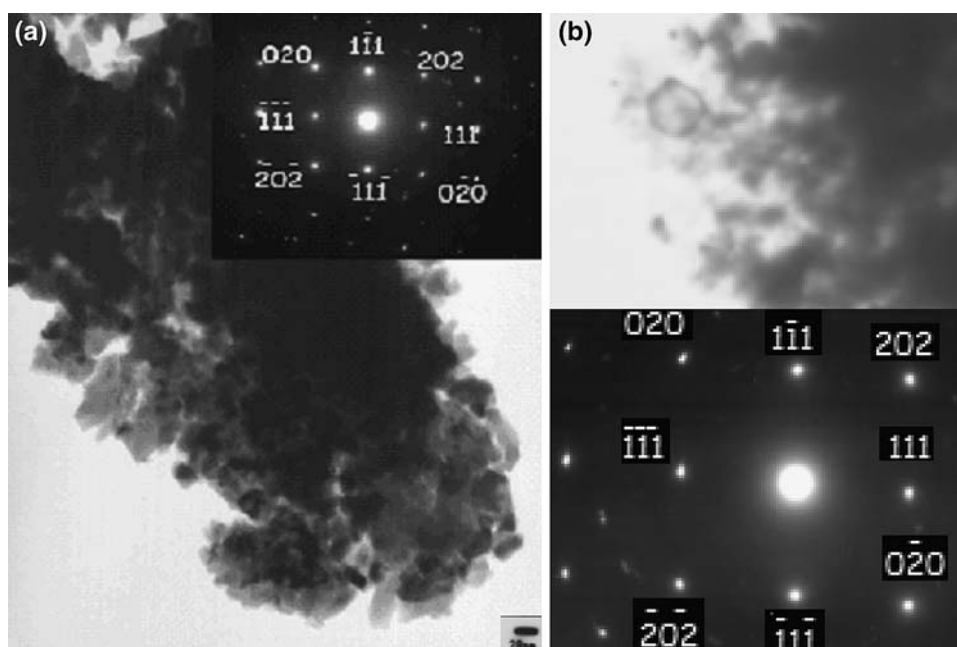


Fig. 14 (a) TEM micrograph powders of YVO_3 compound prepared by sol-gel acrylamide and indexed diffraction pattern of [200] zone axis (left). The scale mark corresponds to 20 nm. (b) TEM of sample prepared by solid state reaction (right). The scale in this case is 1 μm



YVO_4 compound shows a greater homogeneity compared with the samples prepared by solid state reaction. This size homogeneity is preserved in the reduction procedure. Therefore, the YVO_3 sample prepared by sol-gel acrylamide polymerization presents a more homogeneous grain size distribution.

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