



Synthesis and Characterization of Nd:YAG Nanopowder via Polymer DTPA | Metal Chelated Complexes

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Abstract: High transparency ceramic was prepared from Neodymium, Aluminum and yttrium Nd: YAG nano powder. This procedure included preparation of diethylenetriaminepentaacetic (DTPA) followed by polymerization with ethylene glycol. The produced polymer used to form chelated complexes with elements of YAG the formed complexes were calcinated at 600, 700 and 950°C and sintering followed by product under vacuum. The prepared powder was characterized by SEM, ZETA potential, XRD and DTA to make sure of distribution homogeneity of YAG elements (components) (Y₂O₃.Al₂O₃) in crystalline net. The studies showed that prepared polymer produced from DTPA with ethylene glycol enable to bond with Al³⁺, Y³⁺, Nd³⁺ along its chains by chelating, which gives good homogenous powder. The results showed possibility of development of proposed method to give good homogeneity and to graft YAG crystal by Nd with concentration more than 4.8.

Keywords: NdYAG, nano-powders, DTPA, DTPA/metal.

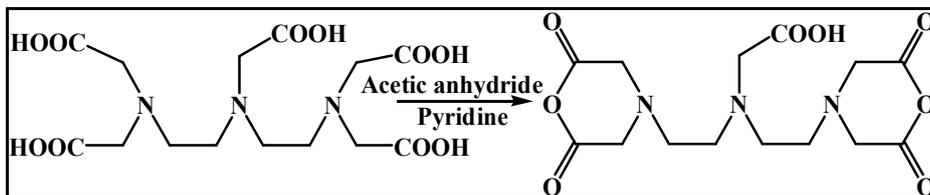
1-Introduction:

The solid-state lasers have been used in scientific, medical, industrial and military applications. The Nd-YAG laser is by far the most commonly used type of solid-state lasers¹. The majority of the Nd-YAG lasers are used Nd:YAG (Y₃Al₅O₁₂) single crystals as active laser materials, due to their high thermal conductivity, chemical stability, good optical quality, high gain and low threshold laser operation^{1,2}. These single crystals are fabricated by Czochralski crystal growth method³. The output of the Nd:YAG laser power strongly depended upon the Nd concentrations in the YAG host matrix. The high cost and the several technical limitations of Nd-YAG crystal fabrication, such as growth of a large size crystal with the high Nd³⁺ doping concentration (>1.5 at.%) in the YAG, have prevented their further development for high power Nd:YAG laser³. The later disadvantage stimulated tremendous efforts for alternative synthesis method. One of these efforts has led to synthesize the polycrystalline Nd:YAG ceramics active laser media, that contained from 1.1 to 4.8 or more at.% Nd doping [1,5] and exhibited nearly the same optical properties as those of a Nd:YAG single crystal¹. In addition, the polycrystalline Nd:YAG ceramics have several advantages such as lower fabrication temperature, shorter fabrication time, allow relatively large doping levels, and large size laser elements^{1,4}. The polycrystalline Nd-YAG ceramics structure could be developed for reaching the best possible homogeneity in their composition and the maximum density. This makes the polycrystalline ceramic laser elements particularly important for the high power laser applications. This is based only upon the gel viscosity for the good homogeneity of the powder components is not sufficient for good powder homogeneity⁸, so one should develop a new method. The aim of this work is to develop a new chelating molecular more powerful with higher homogeneity polycrystalline Nd:YAG nanopowder via polymer DTPA/METAL Chelated complexes.

2- Experimental:

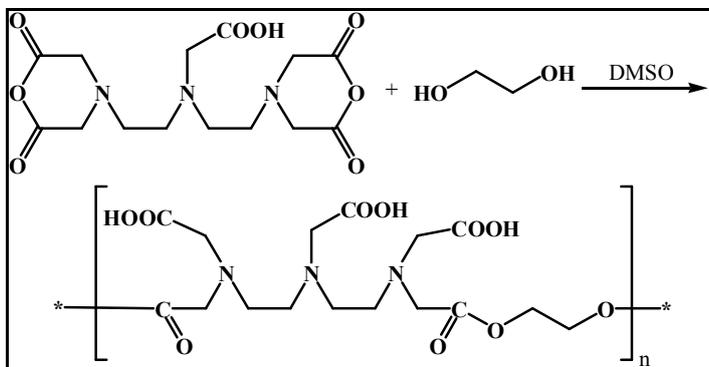
2.1- Material and method:

Nano-sized Yttrium Aluminum Garnet (YAG) powder with average grain size of 100 nm was first obtained by precipitation method using $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98%), $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%) with a molar ratio of 5:3 diethylenetriaminepentaacetic (DTPA) and PEG (polyethylene glycol) were used as chelating/polymerization agent for the sol-gel process can produce the anhydrite by remove two molecular from the end of DTPA in spatial condition at We can produce the anhydrite with this reaction: DTPA (10.0 g, 34 mmol), pyridine (16 mL) and acetic anhydride (14 mL) were placed in a 100 mL-flask equipped with a condenser and a magnetic stirrer. The reaction was carried out at 65-70°C for 12 h. The resulting anhydrite was filtered off and washed thoroughly with acetic anhydride and dry diethyl ether. The white-cream powder was then dried under vacuum at 40-50°C until constant weight was obtained (yield 90- 92%) [Tuelue M. and Geckeler K.E., Synthesis and properties of hydrophilic polymers. Part 7].



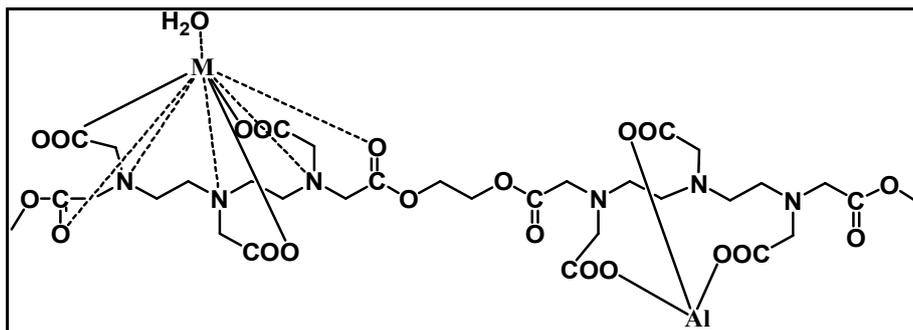
The reaction of Anhydrite DTPA.

Subsequently, where the concentrations of Y and Al were respectively determined by DTPA anhydrite, complexing titration to ensure a desired stoichiometry. According to the nominal composition of $\text{Y}_3\text{Al}_5\text{O}_{12}$ the stoichiometric amount of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ neodymium oxide (Aldrich, 99.99% Nd_2O_3), solution mixture Subsequently the mixture was dropped slowly into a controlled amount of DTPA (dissolved in ammonia) solution under violent and consecutive stirring, in this process, special care should be taken to avoid any precipitation. Therefore it was necessary to add enough ammonium hydroxide to keep the pH of the resulting solution around 6. when a clear and transparent solution was obtained, a certain amount of PEG was added During the process, the molar ratio of DTPA to total metal cation (DTPA/M) was 1:1. and The molar ratio of Al/Y was 5/3 and the stoichiometric ratio of the neodymium was 4.8 at. %Nd. Next the resulting solution was heated by water bathed at 80-90°C to evaporate superfluous water, the volume of the solution decreased and the viscosity increased continuously because of gradual polymerization, when the volume of the solution could not decrease, the solution became a transparent gel with a high viscosity. The polymerization of the anhydrite DTPA with the reaction of DTPA anhydrite with ethylene glycol $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$ resulting complex polymer of Nd-YAG components bonds



The reaction polymerization of Anhydrite DTPA + Al^{+3} , Nd^{+3} , Y^{+3}

That solute by DMSO (dimethylsulfoxide) polar solution. This polymers make possible to form a complex molecular, with the YAG components, that bonded by the chelating with high homogenous medium. The increase of carboxyl functions and the elements containing electronic pairs will increase the ability of polymer to formulate the supporting bonds which leads to much more homogeneity of the three ions.



The complex polymer ions resulted from chelating the 3 ions with DTPA.

Then the gel was put into oven and pre-heated at 180°C for 5h to char the gel. The gel was steamed, boiled, frothed, fumed, finally formed a dry blacksponge (which was called precursor). Due to the evolved gases, the apparent volume expanded greatly after charring and the precursor became so loose that it could be broken into fine pieces easily. Subsequently, this solid precursor was divided into three parts and then respectively calcined in muffle furnace at 600, 700, 950°C for 2h to obtain nano size Nd-YAG powder.

Where, Nd^{+3} , Y^{+3} have coordinate number equals to 9. Eight polymer bonds will be provided and the ninth bonded with the hydrated molecule. The three bonds of aluminum Al^{+3} will be connected with the polymer as shown in the endreaction polymerizations. The presence of great number of free carboxyl groups along the polymer makes its surface active at high potential to dispense any powder, as in the case of CMC (carboxymethyl cellos)^{8,9,13}. The reaction mixture was stirred continuously in a heating bath at 80-90°C under nitrogen atmosphere for 720min. The volume of the solution is decreased and the viscosity increased continuously due to the polymerization. When the solution became transparent gel with high viscosity, it was cooled to the ambient temperature. The pH solution was in the range of 4-7.5 and it was mixed with de-ionized water. The precipitate was filtered, washed with water and then with methanol and finally dried in vacuum. The solid precursor was divided into three parts. and then respectively calcinated in furnace at 600,700,950 °C for about 2hto obtain the nano-sized powders, then after milling at about size 100nm. The powder mixtures were dried and pressed into $\Phi=50$ mm pellets at thickness 3mm, which were further isostatically pressed at 200MPa. The pellets were sintered at 1650°C with heating rate about 15 °C/min in alumina crucible for more than 700 min at vacuum of about 6.10^{-2} Pa and then cooled down to the ambient temperature. The samples were drying (burningthe organic compounds) and then calcinated at different temperatures in order to study the heating temperatures 600,700,950 °C respectively. Three samples were prepared with different rates 1, 2, 5 °C/min. Then the samples were ground in order to get the powder for further ceramic preparation.

2-2-Characterization

pH meter to monitor the change of pH precursor (accuracy of probe 0.01). The phase analysis of the Nd-YAG powder was performed using XRD(Bruker D8 advance) analyzer with $CuK\alpha$ radiation($\lambda=15418$ nm) at 40KV. The phase decomposition and phase transition were detected out using DTA. The microstructure of the Nd-YAG powder and pellets were investigated using SEM (type S-4800,japan. And the zeta potentialwas measured by Malvern Zetasizer 2000.

2-3-Results and discussion:

At pH=7 a large quantity of particles ware precipitated. Buffer solution (pH=7.5) was added to the solution. The increases in pH take place at the starting period of the reaction, then it is stabled during the precipitation. The precipitation starts after pH equal 6 and reaches a value of 7 at the end of the titration process at 300 min

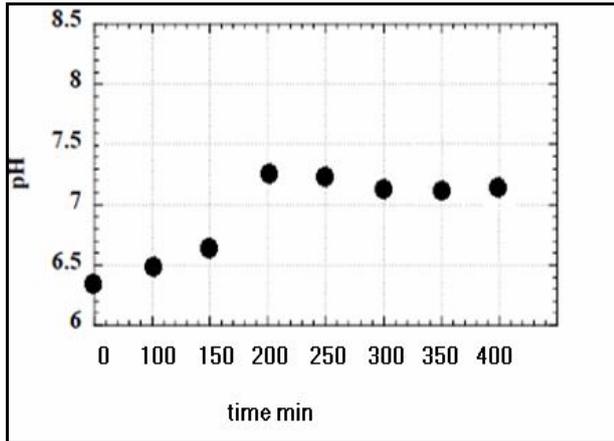


Fig 1 Variation of pH during time

The exact location of the Nd dopants is not fully known¹². Segregation from the bulk towards the interfaces is likely to occur due to the difference in ionic size between Nd (0.995 Å) and Y (0.900 Å), the Nd being substituted on Y sites in the YAG structure¹³. The morphology of Nd:YAG nano-powder as shown in Fig 3 were well dispersed in particles without agglomeration. We used technique, as we mentioned before, Milling to reduce the particle size about 100 nm¹⁶. The potential difference between the shear plane and the solution is called the zeta potential. This potential difference is about -30 to 30 mV. When it is reduced to zero^{17,20}, (the isoelectric point IEP), the particles tend to agglomerate under the influence of the Van der Waals forces and the colloidal suspension becomes destabilized. The zeta-potential of resultant nano-particles. For investigating the pH-sensitivity of nano-particles, which were dissolved in the buffer at value to keep the pH constant during measurement.²⁰

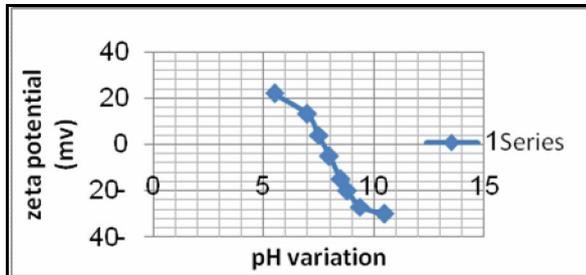


Fig 2- Zeta potential for Nd:YAG nano-powder as a function of pH .Note the particles were dissolved at lower pH.

Zeta potential of precipitated particles was performed, and Figure 2 shows the zeta potential curve of the precipitate particles as a function of pH. The isoelectric points (IEP) for the precipitated powders are shown at pH value of 8. It is known that both zeta potential and electrical double layer thickness are affected by the concentration of ions present in the solution. Thus, changing the synthesis parameters such as Al³⁺, Nd³⁺, Y³⁺ ions concentration will affect the electrical double layer, which will in turn affect the particle growth and eventually size distribution. Although some studies on the synthesis of rare earth oxide particles using homogeneous precipitation by chelating DTPA polymer with have been reported, a proper understanding on the effect of synthesis



Fig 3 SEM at 20kv the polymer DTPA/metal ions (a) (a) at 600 °C, (b) at 700 °C, (c) at 950 °C

parameters on the growth of the particles during precipitation, alumina and yttria particles should attract each other and the particles of the same oxide should repel each other. This situation causes so called hetero flocculation effect which is considered to improve homogenization of the two component powder system¹⁹

3-3SEM Analysis

Fig 3 shows the morphology of the Nd:YAG powder by calcination at 600, 700, 950°C at high temperature. It can reduce the element diffusion between particles. And we can see a decrease in the size of particles of powder with increasing heating. We can see in these three images a smooth surface for the three metal ions with polymer complex. And DTPA polymer is an excellent sorption for various metal ions. Morphology of the thermally etched surfaces of specimens A, B, and C. It can be seen that the average grain sizes, pores, and secondary phase amounts increased versus increasing the heating rate. That is due to the heating rate raising the rapid densification rate of the Nd:YAG ceramics, which obstructs pore exclusion and element diffusion^{17,18}. The average grain size is about 3 μm. Fig 3 (b) shows the average grain size of specimen B is slightly larger than that of specimen A. There are a few pores observed both at the grain boundaries and inner grains, and no secondary phases. As can be seen in Fig. (c), light pores and secondary phases are decreased both along the grain boundaries and inner grains. The results of the present work indicate that the pores and secondary phases of the optical property of Nd:YAG increase with increasing of heating rate. Ceramics is closely related to pores and secondary phases.

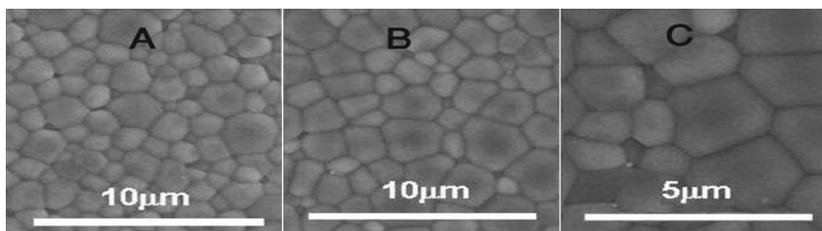


Fig 5 micrographs of specimens A, B, and C image from the thermally etched surfaces of three specimens subjected to 1650°C

3-4-TGA analysis

With starting weight of 100 mg in TG-DTA crucible. The thermogravimetry curve shows that the mass decreased rapidly below 600°C due to removal of organic groups of the polymeric precursor. The thermal decomposition behavior associated with a very large exothermic peak for the sample as seen in the differential thermal analysis curve is suggestive of an auto-ignited combustion process arising from highly exothermic reactions. The endothermic peak at 200°C removal bound water. And the exothermic peak at 920°C, which may be related to crystallization and crystal growth of YAG^{21,22}. As others known this result^{10,15}. And TG curve shows an overall mass loss of approximately quarter its weight.

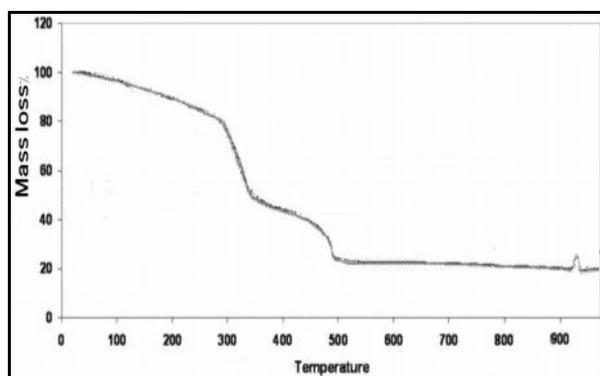


Fig 5 TGA of DTPA polymer heating rate of 5°C/min

3-5 XRD Analysis

X-ray diffraction of the three samples shows the powder XRD patterns of the samples calcined at various temperatures 600, 700, 950 °C for 2h. According to profile the samples are cubic crystalline Nd:YAG.

and with increasing calcinations temperature the peak appear stronger. and we use the XRD to study the characterized degree of Nd:YAG powder

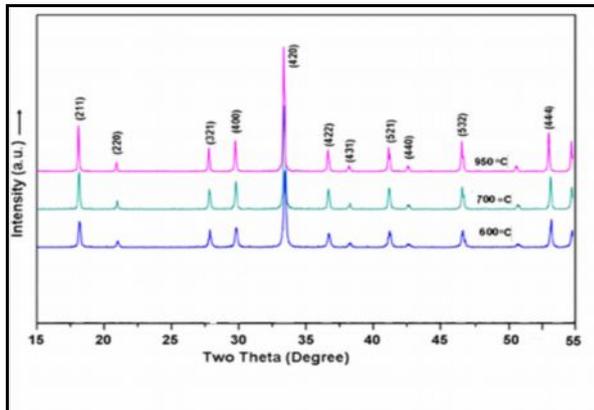


Fig. 5. XRD pattern of the three specimens' powder (prepared by sol-gel method)

4- Conclusions

We depended on a new method to prepare Nd:YAG ceramic from nano-powder, which was fabricated from polymer, DTPA/Metal from 3 ions. characterization included zeta potential, SEM, DTA, and XRD for the specimen showed the homogeneous distribution of the elements ions and calcinated the specimen at 3 temperatures 600, 700 and 950°C was shown eliminate of the atomic agglomeration which produce polycrystalline defects (mainly pores, or secondary phases and agglomeration) and the high homogeneity need a powder where the three elements forming this powder are orderly distributed inside the powder. Then we sintered the three powder at 1700°C. characterization included SEM as in fig 2, TG\DTA as in fig 3 and XRD as in fig 4 for the specimen and we calcinated them at 3 temperatures 600, 700 and 950°C. the results showed the homogeneous distribution of the elements ions in order to eliminate of the atomic agglomeration which produce polycrystalline defects (mainly pores, or secondary phases and agglomeration) that produce defects the laser band specification when using this polycrystalline as laser medium.

6- References:

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