The effects of chelating agent type on the morphology and phase evolutions of alumina nanostructures

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ARTICLE INFO

ABSTRACT

In this work, pure aluminum oxide nanoparticle was obtained by the chemical method at low temperature. In this approach, alpha-alumina nanoparticle was prepared by aluminum nitrate nonahydrate and triethanolamine (TEA) as the Al^{3+} and both gel agent, respectively. FESEM images show that TEA has better efficiency in controlling particle size and agglomeration as compared with citric acid as a chelating agent. Then, yttrium aluminum garnet (YAG) powder was prepared by yttrium nitrate, urea, and tetraethyl orthosilicate (TEOS) as a Y^{3+}, precipitation agent, and flux agent, respectively. Furthermore, results show that by using TEOS, the YAG particles were obtained, while in the absence of this agent, the impurely YAG phase was achieved at the simillar annealing temperature.

1. Introduction

Yttrium Aluminum Garnet is one of the most prominent ceramics with high chemical stability, good optical and mechanical properties. The transparent YAG ceramic has attracted much attention due to its potential applications in laser devices. Alumina nanoparticles and Y-compound is the main precursor of this compound [1]. The alumina has main groups such as aluminum hydroxides and aluminum oxides. The first can be subdivided into two major crystalline kinds of hydroxides: trihydroxides and oxide hydroxides. Three different trihydroxides (gibbsite, bayerite and nordstrandite) and two oxide-hydroxides (boehmite and diaspore) have been identified [2]. Due to the high melting point (T_m > 2040 °C) and low thermal conductivity (10^{-18} W/m·K), alumina have been widely studied [3]. Alumina has different crystal structures, such as δ, η, γ, θ and α phase, etc [4]. When the temperature is increased above- mentioned aluminum crystal structures, finally transform into alpha-Al$_2$O$_3$ [1]. The ultrafine α-Al$_2$O$_3$ powder has significant potential for a broad range of requests for high strength materials, electronic ceramics and catalysts. The wide utilization of ultrafine α-Al$_2$O$_3$ makes it a general material and increases the attentions for the synthesis of ultrafine α-Al$_2$O$_3$ [5]. Due to the broad band gap (Eg=8.5 eV) of this material is applied in optical devices [6] as host materials for luminance application [6–10]. Different chemical methods for the preparation of α-Al$_2$O$_3$ have been described in the kind of literature such as mechanical synthesis [11], vapor deposition [12], co-precipitation [13], combustion [14] and sol–gel method [15]. Some advantages of the sol-gel method are its versatility and the good control of homogeneity, the provision of an easy way for the introduction of trace elements, allowance of the synthesis of special materials and energy savings by using low processing temperature [16,17].

Due to the calcination temperature of above 1000 °C is often needed to produce α-Al$_2$O$_3$, it is difficult to obtain nano α-Al$_2$O$_3$ powder in high calcination temperature. High calcination temperature, unavoidably, leads to a considerable degree of particle coarsening and agglomeration of α-Al$_2$O$_3$ [18]. To solve this problem, triethanolamine (TEA), for the first time, applied as chelate agent. The chelate agent has been found to promote, to slow down, or to prevent crystal growth in solutions [18]. Triethanolamine and citric acid formed polyesterification network. By calcination of this network, nanoparticles were obtained [1].

In the present study, we are presenting the synthesis of α-Al$_2$O$_3$ using the new material triethanolamine by modified Pechini route. Alpha-Al$_2$O$_3$ nanoparticles were synthesized in different proportions of CA, TEA as a chelating agent to obtain different morphologies. Then, by acting TEOS molecules as a phase formation assistant agents, pure YAG phase was achieved at a lower temperature from alfa-alumina nanoparticles.

2. Materials and methods

2.1. Materials

All materials were purchased from the Dae-Jung Reagent Chemicals Company.

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Table 1
Different molar ratios of gel precursor.

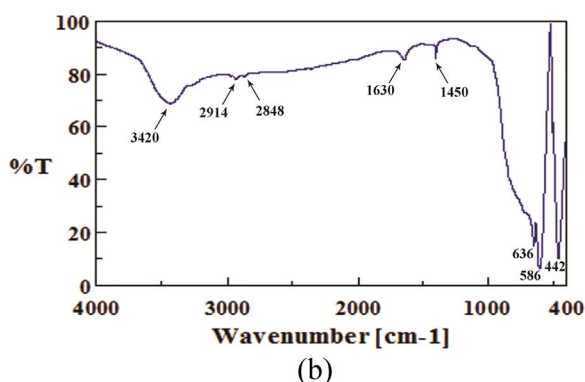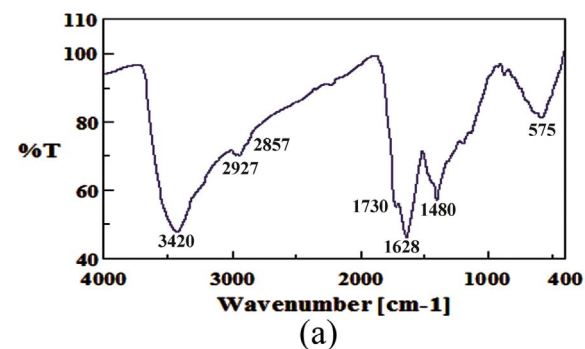| Name	Mol of Al	Mol of TEA	Mol of CA	Mol of EG
A1	1	4	1	–
A2	1	4	4	–
A3	1	4	0	–
A4	1	0	4	–
A5	1	0	4	4

Fig. 1. (a) FT-IR spectra of sample A2 (Al: TEA: CA=1:4:4) before the calcination process. (b) FT-IR spectra of sample A2 after the calcination treatment at 1200 °C.

2.2. Preparation of alumina nanoparticles

According to different molar ratios shown in Table 1 a variety of gels were synthesized. First, aluminum nitrate nonahydrate was dissolved in deionized water and triethanolamine was subsequently added to this solution. Then, citric acid was slowly added to this solution and maintained at 80 °C for 1 h to remove excess solvent. Then, by increasing the temperature to 120 °C for 1 h, the solution became more and more viscous. Finally, xerogel was formed. For complete drying, xerogel was thermally treated at 230 °C for 1 h. the xerogel was placed into the furnace and calcined at different temperatures (800–1430 °C) to obtain alumina nanoparticles.

2.3. Characterization

XRD analysis (X′PertPro model, Panalytical manufacturing Co., Netherlands) with the Cu Kα of 1.789 Å was used. In this test voltage, current, step size, time per step was 40 kV, 30 mA, 0.05 degrees and 2 s, respectively. The differential thermal analysis (DTA) was perfomed on STA-6000, Perkin Elmer under air atmosphere. The FESEM image was taken with TE-SCAN Co. (made in Brno – Kohoutovice, Czech Republic) at the magnification of 50000. The Desk Sputter Coater (Nanostructured coating Co., DST3 model, Iran) was used for gold sputtering of the samples. The PL spectra were taken on a RF-5301PC spectrophotometer (Shimadzu, Japan, stimulated by irradiated light with $\lambda_{excitation}$ =255 nm).

3. Results and discussion

3.1. Fourier transform infrared (FTIR)

The FTIR spectrum of dried gels (A2 sample) is demonstrated in Fig. 1(a). Triethanolamine is a tertiary amine and has three alcohol group. Citric acid is a weak tribasic acid molecule. As you know, by the combination of acid and alcohol, an ester is formed, by heating ester solution, the polymer network or gel is formed. The band at 1730 cm^{-1} is assigned to the C=O stretching mode of the ester. The absence of this peak in another sample implies that polyester gel network is not well formed. As can be seen in Fig. 1(a), the broad band around 3420 cm^{-1} and 1628 cm^{-1} are belonged to the hydroxyl (-OH) stretching modes and bending modes of adhesive and structural water, respectively. The band observed at 1480 cm^{-1} corresponds to Al−OH vibration [19]. Strong absorption bands at 575 cm^{-1} are related to the Al−O bond [20]. The peaks at 2927, and 2857 cm^{-1}, are assigned to asymmetric and symmetric stretching of CH$_2$, respectively [21].

Fig. 1(b) shows sample A2 after calcination in 1200 °C. After calcination, a large percentage of organic substances are removed. According to Fig. 1(b), the − OH related peaks in 3420 cm^{-1} and 1630 cm^{-1} became weaker at 1200 °C as compared to Fig. 1(a).
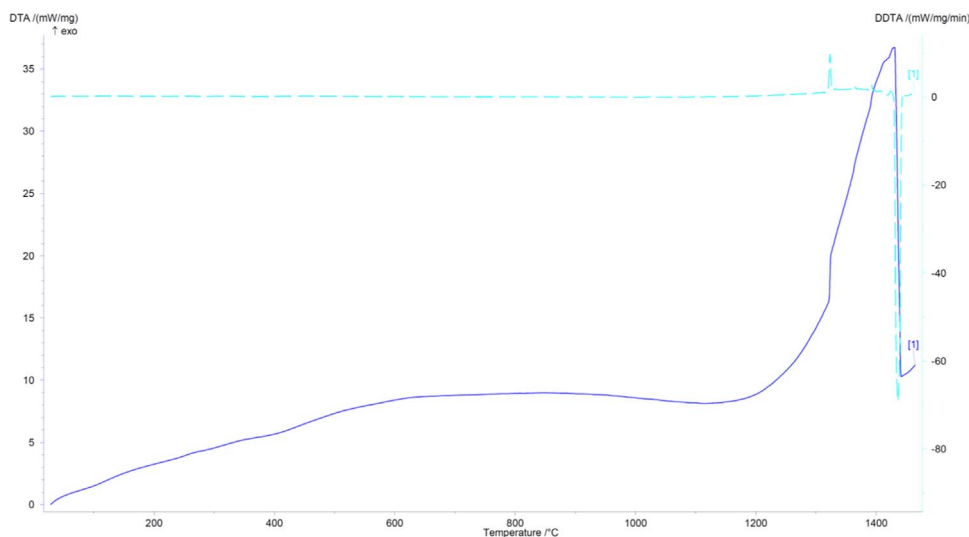

Fig. 2. DTA–DDTA curve of the gel A2 prepared by the use of Al: TEA: CA=1:4:4 mol ratio.