

Yttria Nanoparticles Prepared from Salicylic Acid-Y(III) Nanocomposite as a New Precursor

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Authors' contributions

This work was carried out in collaboration between all authors. Author MR designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors SM, MY and AS managed the analyses of the study. All authors read and approved the final manuscript.

Research Article

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ABSTRACT

A novel method for the fabrication of high purity yttria, Y_2O_3 , nano-particles is presented by thermal decomposition of salicylic acid-Y(III) nano composite as precursor. The nano composite was formed by a sonochemical method from the reaction between Y(III) nitrate hexahydrate, potassium thiocyanide, KSCN, and 2-hydroxyl benzoic acid, (salicylic acid = sal) in ethyleneglycol, eg, under ultrasonic irradiation with the rated output power of 600 W and frequency 20 KHz. Characterization of the mentioned compound was performed by FTIR spectroscopy, elemental analysis, scanning electron microscopy (SEM) and thermal analysis, TG/DTA. Yttria, nanoparticles were prepared by thermal decomposition of the nano composite at two different conditions in ambient atmosphere. The product was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and fourier transform infrared (FT-IR) spectroscopy. The purity of Y_2O_3 nano-powder tested by ICP-AES analysis is 99.99%.

Keywords: *Yttrium oxide; electrolyte; solid oxide fuel cells; salicylic acid.*

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1. INTRODUCTION

Yttria or yttrium oxide is an air stable and important inorganic compound with many potential applications such as high temperature superconductor, $\text{YBa}_2\text{Cu}_3\text{O}_7$ [1,2]. Yttria-stabilized zirconia, also called YSZ, is currently the most important ceramic oxygen ion conducting material. It is used in the anode and the electrolyte of solid oxide fuel cells (SOFC), oxygen gas sensors, and oxygen pumps [3-5]. Yttria, Y_2O_3 , doped zirconia stabilize the cubic crystal structure of the zirconia down to room temperature, avoiding the phase transitions that pure zirconia undergo during heating or cooling [3]. Also Y_2O_3 europium phosphors gives the red colour in colour TV picture tubes [6,7], and stabilization of the conductive cubic fluorite phase, for increasing ionic conductivity [5,8].

Li Ling in 2005 has published a synthetic route for preparation of Y_2O_3 nanoparticles from solution of industrial YCl_3 using method of oxalate precipitation [9]. Many different synthetic approaches have been reported for the synthesis of nano-structured material such as chemical vapor deposition, chemical bath deposition, hydrothermal, homogeneous precipitation in an organic matrix and sonochemical methods [10-15]. Yttria has been prepared by a number of synthetic methods such as hydrothermal and solvothermal synthesis, precipitation techniques and thermal decomposition [16-19].

As sal, sal = salicylic acid, can act as mono or bidentate ligand, in which phenolate and carboxylate groups can be coordinated depending on the charge/radius of the metal ion and pH range [20-22], we used it as stabilizer for synthesizing of Y(III) nano composites.

In this study we synthesized a new Y(III)-sal nano composite via sonochemical method in 30 min only. It is Thermal decomposition of the nano composite, leads to the formation of yttrium oxide spherical nanoparticles, also we investigated the influences of calcinations condition on morphology and particle size of the produced nano yttrium oxide.

2. EXPERIMENTAL DETAILS

All reagents and solvents for the preparation and analysis were commercially available and were used as received. Infrared spectra were measured with a FTIR spectrometer (4000-400 cm^{-1}) on a Bruker tensor 27 spectrometer in a KBr matrix. X-ray powder diffraction (XRD) measurements were performed with monochromatized CuK_α radiation using a Philips diffractometer manufactured by X'pert. The diffractogram was recorded in terms of 2θ in the range $0-90^\circ$. The samples were characterized with a scanning electron microscope (SEM) and energy dispersive X-ray (EDX) techniques (Philips XL30) with gold coating. A multi wave ultrasonic generator operating at 20 KHz with a maximum power output of 600 W.

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. The samples were coated with gold for SEM characterization. Elemental analysis was performed using a Perkin Elmer 2400 SERIES (II). The compound was heated in ambient atmosphere from 10 to 600°C , with a heating rate of $10^\circ\text{C}/\text{min}$.

2.1 Preparation of Yttrium Oxide Nanoparticles

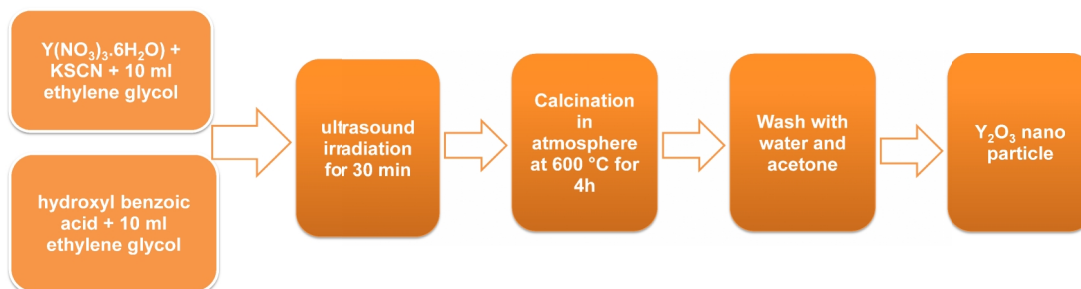
Salicylic acid (0.5 mmol, 0.07 g) was dissolved in 10 ml ethylene glycol. Then yttrium (III) nitrate hexahydrate (0.5 mmol, 0.2 g), and potassium thiocyanide (1 mmol, 0.1 g) dissolved in 10 ml ethylene glycol solution. Two solutions were placed in an ultrasound vessel under

powerful ultrasound irradiations for 30 min (Amplitude: 70, energy: 54.132, frequency: 20 KHz). This reaction was carried out under room temperature and ambient pressure. A white precipitate of Y (III) product was filtered after centrifuging at 4000 rpm for 15 min. The precipitate was washed with double distilled water and followed with acetone respectively. The resulting white powder was 0.156 g. (Decomd. at $> 300^{\circ}\text{C}$. Anal. Calcd for $(\text{Y}_2\text{sal}_6\text{eg}_2)$: Y, 15.71%; C, 49.48%; H, 3.71%; O, 31.10%. Found: Y, 15.70%; C, 49.47%; H, 3.70%; O, 31.00%. FTIR (KBr) spectrum exhibits a complicated pattern of bands in the range $400\text{--}4000\text{ cm}^{-1}$: $3500\text{--}3000(\text{b})$, $642(\text{sh})$, $1630(\text{s})$, $1485(\text{w})$, $1250(\text{w})$, $750(\text{s})$, $569(\text{sh})$, $478(\text{w})$). belong to characterization.

In order to prepare the Ytria nanoparticles, the white powders of the Y(III)-sal nano composite (0.1 g) was calcinated at 600°C and 1000°C (explain briefly why using 2 temperature sets) for 4 hours, in ambient atmosphere, respectively. The product was washed with double distilled water and acetone respectively. The product was separated by centrifuging at 4000 rpm for 15 min. Y, 78.74%. Found: Y, 78.73%. FTIR (KBr) spectrum of Y_2O_3 , prepared at 1000°C for 4 h, in the range $400\text{--}4000\text{ cm}^{-1}$: $3439(\text{b})$, $2923(\text{w})$, $2853(\text{sh})$, $1627(\text{w})$, $1532(\text{w})$, $1398(\text{s})$, $568(\text{s})$, $495(\text{w})$.

3. RESULTS AND DISCUSSION

Scheme 1 shows the processes for the synthesis of Y(III)-sal nano composite and its conversion to Y_2O_3 by calcinations. The current synthetic procedure is a method developed by Morsali group for the synthesis of various nanoparticles of metals, metals oxides, metal sulfides, and metal halides which employ the thermal decomposition of coordination polymers [14]. The Y(III)-sal nano composite were prepared by ultrasonication of the ethylene glycolic solution containing yttrium nitrate and sal.



Scheme 1. Synthesis of yttria nano particles block diagram.

The characterization of the resulting Y(III)-sal nano composite was performed using melting point, elemental analysis FT-IR spectroscopy.

The melting point was different from starting materials. The melting points were 100°C and 159°C for $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and Sal respectively, while the new nano composite decomposed at $>300^{\circ}\text{C}$. The elemental analysis showed that the C, H, O and Y contents was different from known complexes, $[\text{Y}_2(\text{C}_7\text{H}_5\text{O}_3)_6(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ [21], and $[\text{Dy}(\text{sal})_3(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ [22], and $\text{RE}(\text{Hsal})_3 \cdot 2\text{H}_2\text{O}$, ($\text{RE} = \text{EU}$, Y , and $\text{Hsal} = \text{C}_7\text{H}_5\text{O}_3$), Y(III)-sal through deprotonated carboxylate oxygen of sal, either in (1:1) or (1:2) mole ratios. The existence of protonated complexes, YHL_2^+ and $\text{Y}(\text{HL})^{+2}$ were varied by calculations [20]. Proposed formula based on

the results of elemental analysis data is matched with the chemical formula, $[Y_2 (C_{46}H_{42}O_{22})] = \{Y_2 (C_7H_5O_3)_6[(C_2H_4) (OH)_2]_2\}$.

FT-IR spectroscopy is a useful tool to understand the functional group of any organic molecule. The presence of the salicylate group on the Y nano particles is indicated by COO vibrational mode. As a result of composite formation, the broad band appearing in the 1657-1611 cm^{-1} region, which is a typical peak of salicylic acid due to the C=O stretching in aromatic carboxylic acids, is absent in the FTIR spectrum of the produced Y(III)-sal nano composite. The carbonyl group stretching mode is shifted to lowered wave numbers, 1630 cm^{-1} , and OH vibration bands are changed. The vibration bands in 569 and 478 cm^{-1} may be due to Y-O bonds. However, the broad, intense bands observed around 3300 cm^{-1} were attributed to an O-H stretching vibration. Above band verification shows that Y (III) ions are coordinated by the oxygen atom from the COO group, rather than by the oxygen atom from O-H.

Fig. 1 shows that above bands (which bands? Please specify them) disappeared after the calcination procedure. The characteristic bands of COO and OH groups also disappeared showing only strong bands due to the Yttrium oxide. The strong peak at 566 and 473 cm^{-1} is due to the Y-O vibrations, indicating formation of Y_2O_3 .

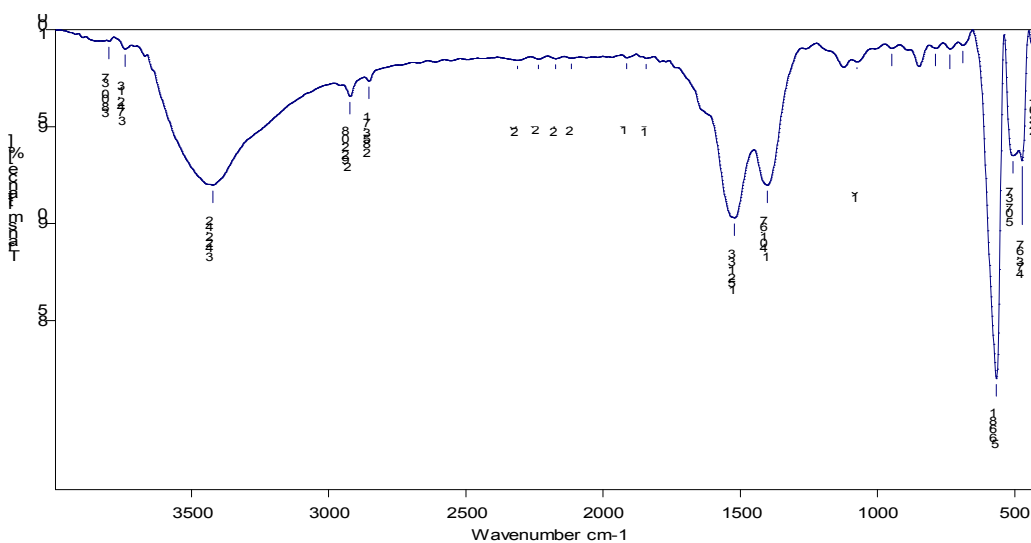


Fig. 1. IR spectrum of Y_2O_3 nano particles prepared at 500°C

Fig. 2 represents the scanning electron micrograph, SEM, of the Y (III)-sal nano composite. This micrograph reveals that the nanoparticles have uniformity in shape and size with spherical morphology. As a result, the nano particles aggregate randomly to form almost spherical shape. The average size of the particles was observed to be around 80 nm.

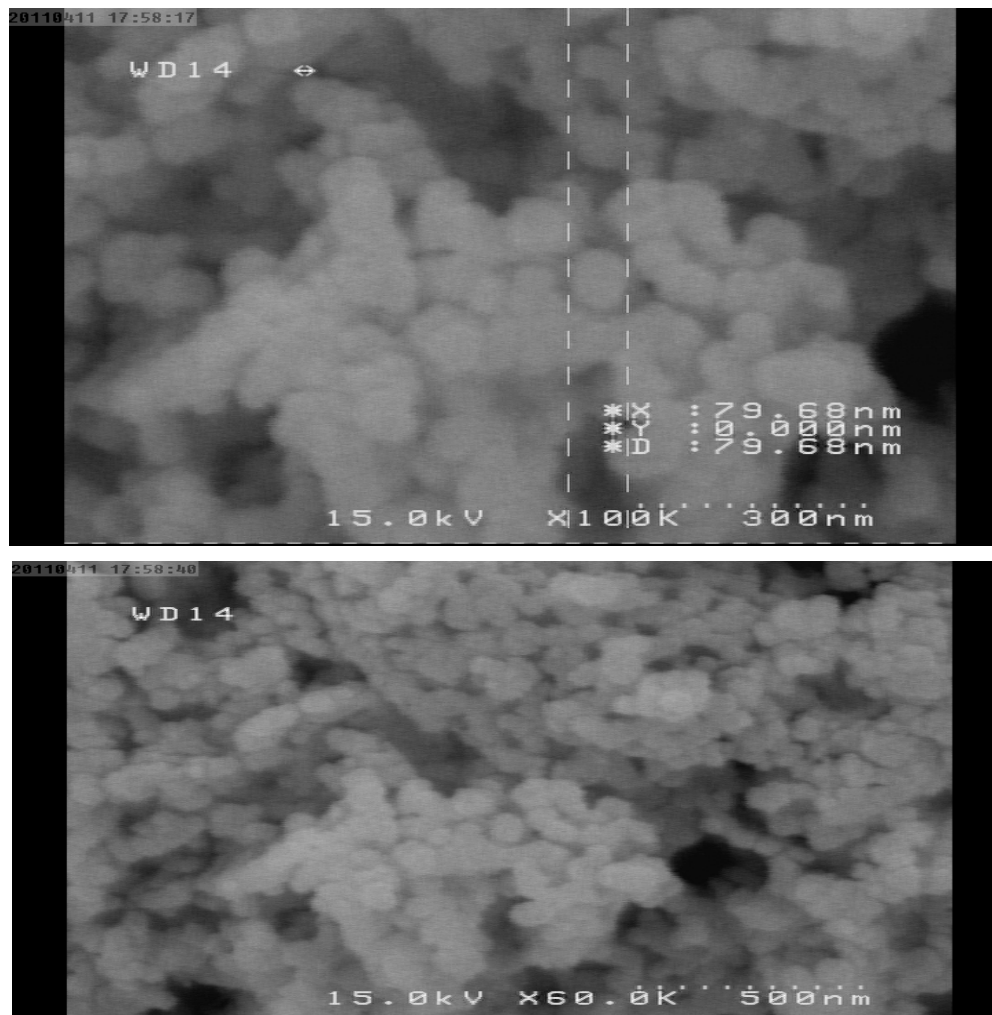
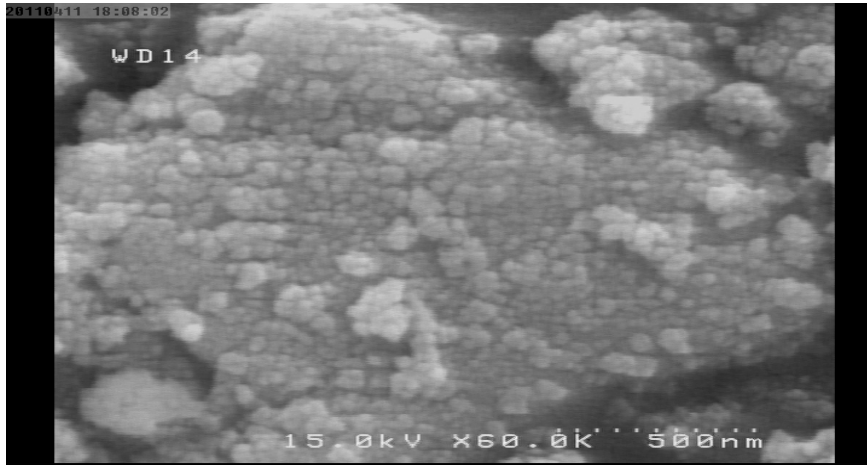


Fig. 2. The SEM micrograph of Y (III) salicylate nano composite

Nano particles Y_2O_3 has been generated by thermal decomposition of Y(III)-sal nano composite at two different temperatures, in 500°C and 1000°C under ambient atmosphere (Figs. 3a and 3b). The morphology and size of the Y_2O_3 particles were further investigated using SEM. SEM characterization indicated that the particles of yttrium oxide calcinated under 500°C are around 50nm while the Y_2O_3 calcinated under 1000°C are around 80 nm. Calcination at 1000°C yields larger size particles than at 500°C. It can also be observed that particles treated under 1000°C has sharper edges than those treated under 500°C. This confirm higher level of crystalline at 1000°C (Fig. 4b).

However, XRD characterization (Fig. 4) shows identical pattern for samples calcinated at 500 and 1000°C. The obtained XRD patterns are consistent with a literature reported data measured on a high crystallites of Y_2O_3 . (Cite the literature here) This proved that the obtained Y_2O_3 is standard cubic structure. Table 1 summarizes the XRD pattern results of Y_2O_3 nano particles.

a) 500°C



b) 1000°C

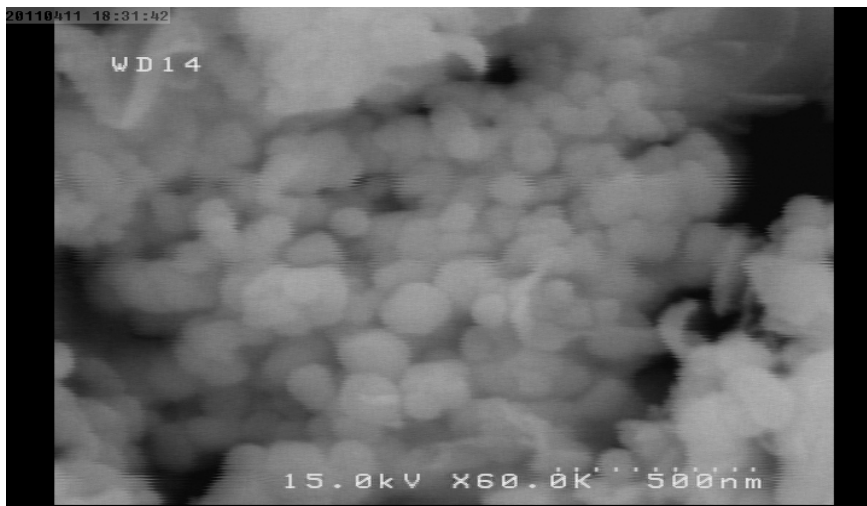
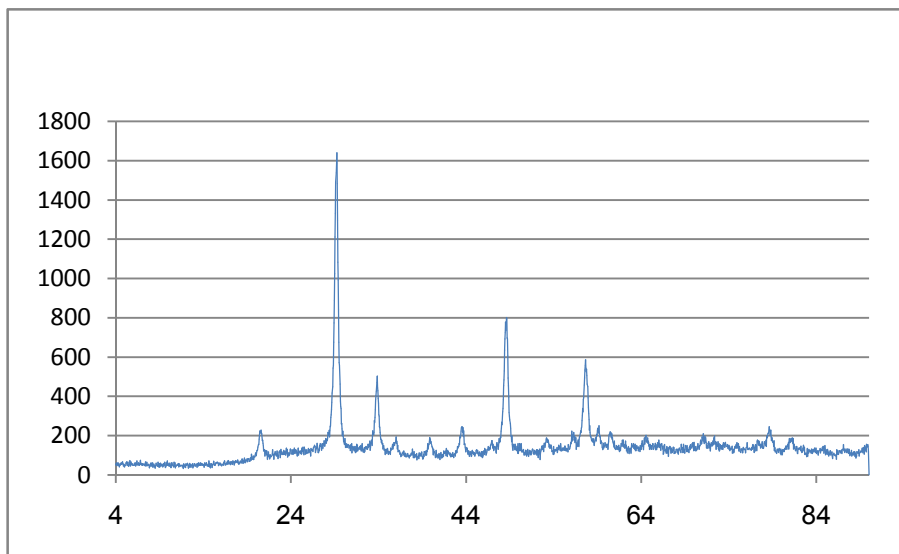


Fig. 3. SEM micrographs of Y_2O_3 nano particles (produced by calcinations of Y (III)-sal nano composite) at 500°C (a) and 1000°C (b)

Table 1. Assignment of miller indices to Y_2O_3 nano particles

Sr. No.	2 θ degree	hkl
1	29.00	111
2	33.70	200
3	48.33	220
4	57.33	311

a) 500°C



b) 1000°C

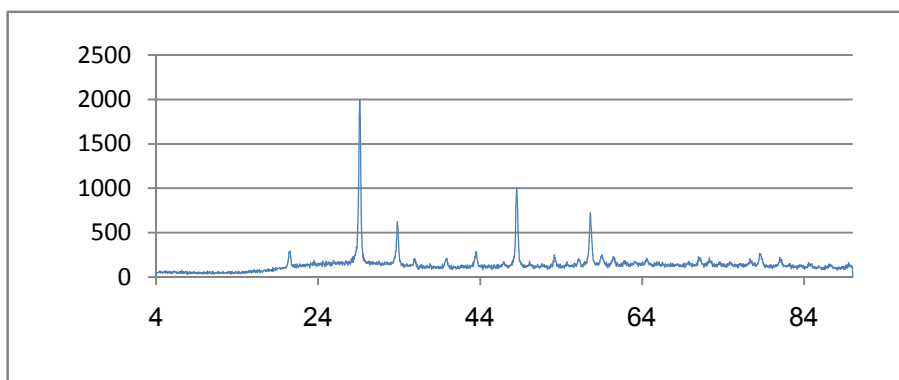


Fig. 4. XRD pattern of synthesized Y_2O_3 nano structures a) 500°C b) 1000°C

Thermal gravimetric (TG) and differential thermal analysis (DTA) were carried out from 10 to 600°C in an ambient atmosphere (Fig. 5). Decomposition of the compound starts from 74°C and ends at 733°C. Between this temperature range, the weight loss may be due to the removal of the ethylglycol and sal ligands. At temperature higher than 733°C, residual compounds, probably Y_2O_3 , stop losing weight, but grow their sizes, as showed in SEM characterization images. Based on TG/DTA analysis, production of Y_2O_3 probably occurs after 500°C. As thermal decomposition was take placed during 24 h at 1000°C, the Y_2O_3 nanoparticles have been grown, and the particle sizes increased.

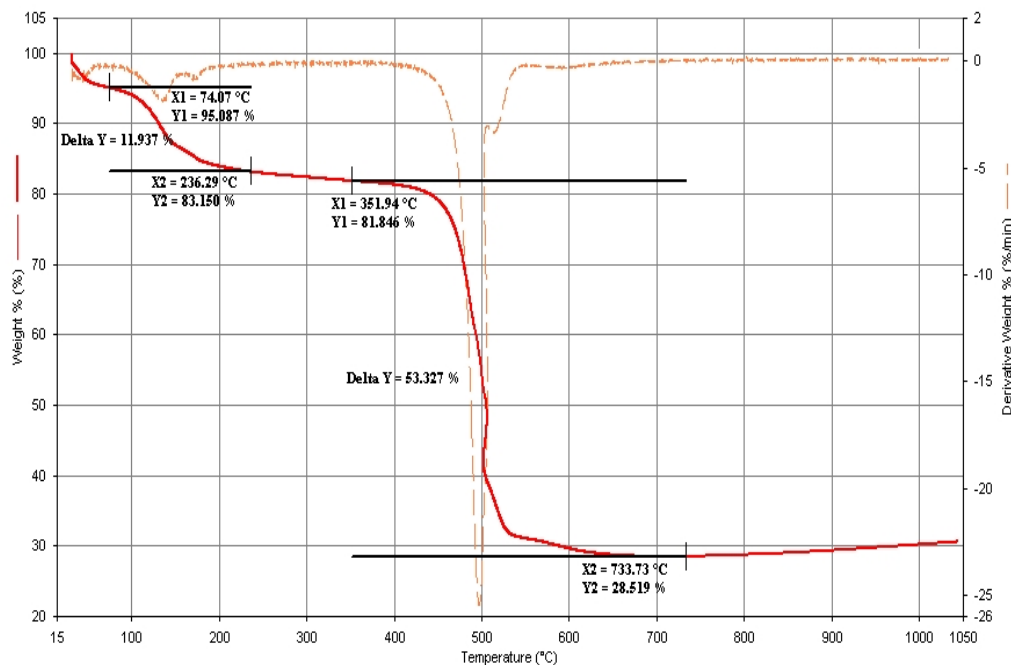


Fig. 5. TG/DTA diagrams of Y (III)-sal nano composite

4. CONCLUSION

A new Y(III)-sal nano composite has been prepared from the reaction between salicylic acid in ethylene glycol as solvent and yttrium nitrate hexahydrate via sonochemical method. The particle size of the product is around 79 nm. Thermal decomposition of the nano composite under 500 and 1000°C leads to the formation of yttrium oxide with cubic crystal system. The size of Y_2O_3 crystals increases while calcinations take place at higher temperatures. Morphology of nano Y_2O_3 is affected by its starting nano composite Y(III)-sal, both of them have almost spherical shaped. This method produces good yield in a short reaction time of 30 min, and no needs to high temperatures or high pressures respect to traditional methods which demands high temperature, i.e. >>1000°C.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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