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SYNTHESIS AND CHARACTERIZATION OF NANO-$BaTiO_3$ POWDER BY A HYDROTHERMAL METHOD

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Abstract- ***Nano - $BaTiO_3$ powders were synthesized using the hydrothermal method. During the synthesis, titanium isopropoxide, isopropanol and barium acetate were used as the main raw materials. The suspension reacted hydrothermally in a teflon vessel at 200 ºC in1 h.***
These modified $BaTiO_3$ powders were characterized by several different methods; FT - IR, XRD, BET, SEM and thermogravimetric analysis and differential thermal analysis (Tg - DTA) . The phase purity and crystalline structure of $BaTiO_3$ was determined using an X - ray diffractometer (XRD) with Cu Kα radiation. According to the X-ray diffraction analysis, $BaTiO_3$ nano powders have cubic $BaTiO_3$ phases at room temperature. The SEM results revealed that the morphologies and the sizes of the synthesized $BaTiO_3$ particles hadan accelerating voltage of 20 kV. The particle size of $BaTiO_3$ was calculated as 18.97 nm (for the λ = 1.54056 Å), using the Schreer equation. The average pore diameter was measured using BET analysis and the pore size was found to be 33.6424 nm.

Keywords - Hydrothermal method, nanoparticles, $BaTiO_3$

I. INTRODUCTION

Barium titanate (BT) is a well known ferroelectric material. Due to its specific electrical properties, lots of studies have been conducted by several different groups in the last six decades. It has a wide application range, consisting of dielectric material in multilayer ceramic capacitors – MLCC [1], positive temperature coefficient of resistivity- PTCR [2], thermistors, piezoelectric sensors/ actuators, optoelectronic devices, transducers, actuators, etc. [1,3], electroluminescent panels, pyroelectric detectors, embedded capacitance in printed circuit boards, sensors, controllers and pulse generating devices [1] and dynamic random access memory (DRAM) [4]. $BaTiO_3$ powders have been synthesized through different techniques e.g the hydrothermal method [5,6], sol-gel processing [7] the oxalate route [5], microwave heating [5], a micro-emulsion process [5], a polymeric precursor method [5], ball milling, solid-state reaction [6,8], solvothermal [6] and different chemical routes [6].

Each method has its own advantages and disadvantages. For example, the solid state reaction method requires heating temperatures as high as 1200 ºC [9,10]. It is stated that high temperatures cause the formation of agglomerated crystallites in different sizes [4,11]. In contrast, the hydrothermal synthesis needs a lower processing temperature, between 100 – 250 ºC [12-15] but higher pressure. In addition, the hydrothermal synthesis yields relatively uniform particles with narrow size distributions [8]. Ultrafine, high purity, homogeneous and ultra - fine $BaTiO_3$ nanoparticles can be obtained via low temperature synthesis [5,13,14]. According to the configuration of the hydrothermal equipment, powder with different particle sizes, ranging from the nanometer to centimeter, can be synthesized [14]. BT powder forms were altered from a cubic shape to a tetragonal shape [13] if the applied temperature was increased to 1000 ºC.

Nano-BT can easily be produced using the hydrothermal method with barium acetate and titanium iso - propoxide. The purpose of this study is to synthesize and characterize fine BT powders through the hydrothermal method.

II. THE CHEMICALS AND APPARATUS

Titanium-iso-propoxide ($Ti(OPr^i)_4$, 97%) from Alfa Aesar (www.alfa.com), Barium acetate ($Ba(CH_3COO)_2$, 99%) and tetrabutyl-ammonium hydroxide (TBAH, 40% solution in H_2O) were purchased from Sigma-Aldrich (www.sigmaaldrich.com). i-Propanol was purchased from Riedel de Haen, (99%) (www.riedeldehaen.com) as a solvent. The solvent was dried with molecular sieve (Fluka, 3A° XL8) (www. sigmaaldrich.com) before use. All other chemicals used were of analytical grade and no further purification was needed. Deionized water was used for the hydrolysis of $Ti(OPr^i)_4$.

The crystalline phase of the nano-composites particles was analyzed using an X-ray powder diffraction (XRD) pattern obtained from Rigaku Geigerflex D Max / B diffractometer, and had a Cu Kα radiation (λ = 0.15418 nm) in the region 2θ = 10 – 90° with a step size of 0.04°. The crystallite size of the anatase particle was calculated from the X - ray diffraction peak using Scherrer's equation. SEM (LEO EVO

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40) was used to examine the surface morphology. The BET surface area and average pore diameter was determined using ASAP 2000 model BET analyzer. The BET surface area, average pore diameter and micropore volume of the nano-composites were calculated from the N_2 adsorption isotherm at liquid N_2 temperature. The sample was degassed at 130 °C for 4 h before N_2 adsorption. Pore size distribution of the nano-composites was computed using the DFT plus method. FT - IR spectra were collected using Perkin Elmer Spectrum One FT - IR Specktrometer. FT - IR measurements of the samples were carried out in transmission mode from 700 cm^{-1} to 4000 cm^{-1} with ATR unit.

The thermal behaviour of the nanocompozites was observed using the thermogravimetric analysis system (TGA, Labsys). This experiment was performed using nearly 10 mg of powder in alumina crucible, which was heated to 1200 °C at 20 °C min^{-1} in dry argon gas, flowing at 40 ml / min. The analysis was conducted by recording celestite coke mixture mass change against temperature and using a Setaram Labsys S60 model TGA instrument, which enables measurements to be performed within a temperature range of ambient to 1600 °C

III. PREPARATION OF NANO-COMPOSITES

$Ti(OPr^i)_4$ was dissolved in i - propanol and stirred with a homogen mixture of $Ba(OAc)_2$ / TBAH for 10 min at room temperature. The mole ratios of $Ba(OAc)_2$: TBAH and $Ti(OPr^i)_4$: $Ba(OAc)_2$ were 1 : 2 and 1 : 1, respectively. The pH of the blend was adjusted to 13 via TBAH. Then, the homogen mixture was transferred into a stainless steel Teflon-lined autoclave and heated at 200 °C for 1 h. The nanocompozite and solution were separated through centrifugation and dried in a vacuum sterilizer at 40 °C for 4 h. Afterwards, the nanocomposite powder was obtained.

IV. RESULTS AND DISCUSSION

The crystalline phase of the hydrothermally synthesized nano-composite was analyzed by XRD. Figure (1) shows that the XRD pattern of nano composite BT have sharp peaks at 22.159, 31.340, 38.718, 44.941, 55.921 and 65.539 2θ values. The corresponding lines of cubic phase are (1 0 0), (1 1 0), (1 1 1), (2 0 0), (2 1 1) and (2 2 0) [16,17]. The size of the BT crystals were calculated through the well-known Scherrer's equation and the average crystal size was found to be 18.97 nm.

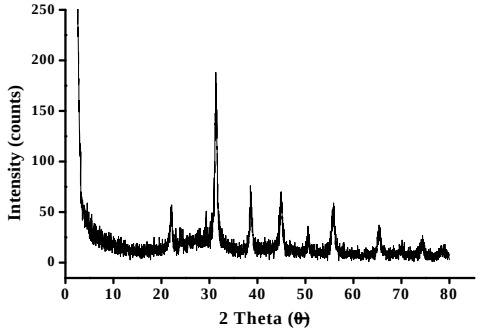

Fig. 1 XRD pattern of the nano- composite

The BET surface area, average pore diameter and micropore volume of the nano-composite was calculated from a N_2 adsorption isotherm obtained at liquid N_2 temperature, where the sample was degassed at 130 ºC for 4 h before N_2 adsorption. It was found that the BET surface area, average pore diameter and micropore volume was 23.78 m^2 / g, 33.64 nm and 0.0023 cm^3 / g, respectively in Fig. 2. According to the result of the DFT plus method, mesoporosity dominated and was distributed in the range of 8-80 □. The mesoporosity (percentage of mesopores to total pore volume of the pores less than 101.68 nm, Vme / Vtot) was 98.06%. The macroporosity (percentage of macropores to total pore volume, Vmi / Vtot) was 1.94%.

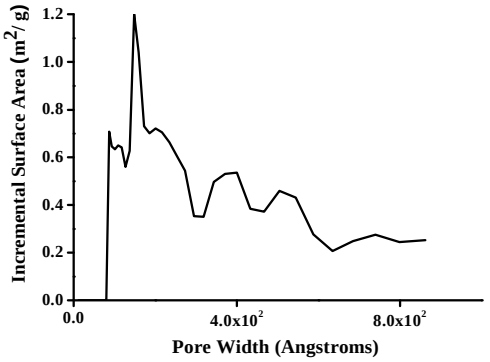

Fig. 2 BET of nano-composite

The BT nano-composite group, synthesized hydrothermally, was analyzed using FT - IR. The interaction between the $BaTiO_3$ nanocrystals was explained by the FT - IR spectrum. Figure (3) shows that the main bands are in the range from 3600 cm^{-1} to 3000 cm^{-1} , due to the stretching vibrations of OH^- groups [18,19]. The strong absorbance at 1424 cm^{-1} and 1563 cm^{-1} can be attributed to the CO symmetric and asymmetric stretch vibrations of the deprotonated carboxylate group, respectively [18]. The strongest peaks at 2876 cm^{-1} and 2961 cm^{-1} were due to the C – H symmetric and asymmetric stretch vibrations of the – CH_2 and – CH_3 groups in organic alkyl [18,19].

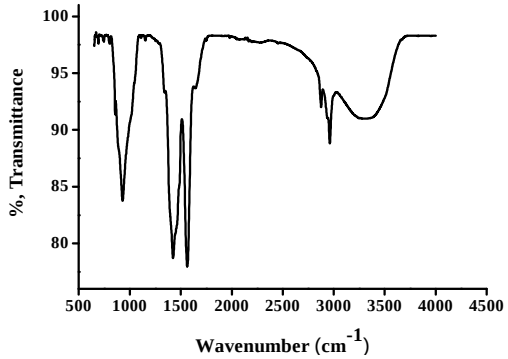

Fig.3 Typical FT-IR spectrum of synthesized nBT particle

The typical SEM images of BT particles shown in Fig. 4 indicate that the shape of the particles are similar to each other and likely to become spherical and agglomerate.

The rates of mass loss derived from Fig. 5 are also shown in the form of Tg-DTA traces and exhibit reaction regions more clearly. There are only two peaks for the nano $BaTiO_3$; the first one, which was observed at 152 °C, refers to the evaporated water from the sample or low – molecular – weight - organic species [20,21]. The second peak appeared at 351 °C, and was responsible for the pyrolysis of acetate [22]. Thermal separation was nearly completed below 600 °C.

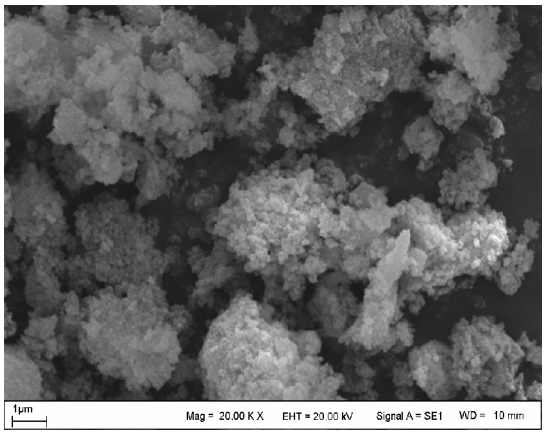

Fig. 4 Typical SEM microphotograph of hydrothermally synthesized $BaTiO_3$

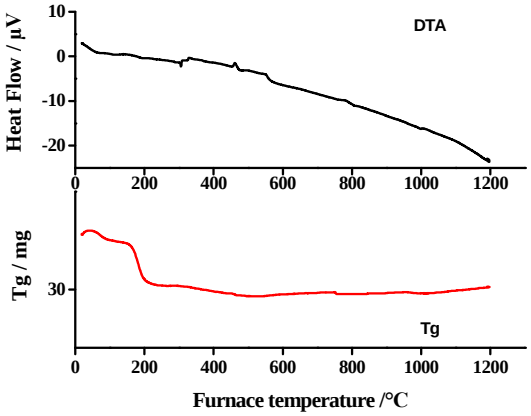

Fig. 5 Tg - DTA of nano - composite

V. CONCLUSIONS

In this paper, Barium Titanate (BT) was synthesized by a hydrothermal process at 200 ºC in 1 h. The structure of BT was analyzed through several different methods; FT - IR, XRD, SEM, BET, and Tg - DTA. Spherical and cubic crystal nano-powders can be obtained using the experiments previously described. We deduced that the hydrothermal process required shorter experimental time and lower temperatures compared to the other techniques. Therefore, the hydrothermal method could provide a better means to analyze the BT structure. The other properties need to be further investigated.

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