

Preparation and Characterization of Barium Carbonate Nanoparticles

Amir Zelati, Ahmad Amirabadizadeh, and Ahmad Kompany

Abstract—In this research barium carbonate nanoparticle with composition BaCO_3 (Witherite) was prepared by using the gel-combustion (sol - gel) method. A precursor sol was obtained from barium nitrate. The molar ratio of citrate/nitrate=1.3 (CA/NO-3 =1.3) was used to prepare very fine powders of barium carbonate. The gels resulting from these sols were transformed into powders by an auto-combustion process at $\leq 400^\circ\text{C}$. The powders consisted of orthorhombic BaCO_3 and one another additional phase. The barium carbonate nano-particles produced by the gel-combustion method were calcined in three different calcination temperatures $T = 450^\circ\text{C}$, $T = 600^\circ\text{C}$ and $T = 750^\circ\text{C}$. The pure orthorhombic phase was found at 450°C X-Ray diffraction. The effect of calcination temperature was studied in three various temperatures. The crystallite size XRD was estimated from the broadening of XRD peaks, using Scherrer's formula. Transmission electron microscope (TEM) and X-Ray diffraction (XRD) of the samples were used for characterization of the obtain products. The size of particles were produced by this method are between 1nm to 10nm.

Index Terms—Barium Carbonate, Gel-Combustion Method, Nanoparticle, TEM, XRD, Scherrer's Formula.

I. INTRODUCTION

Barium carbonate (BaCO_3), also known as Witherite, is an important material in industry for producing barium salts, pigment, optical glass, ceramic, electric condensers, as well as its close relationship with aragonite, biomineral and its use as a precursor for magnetic ferrites and/or ferroelectric materials. Witherite crystallizes in the orthorhombic system. The crystals are invariably twinned together in groups of three, giving rise to pseudo-hexagonal forms somewhat resembling bipyramidal crystals of quartz, the faces are usually rough and striated horizontally [5, 6].

The mineral is named after William Withering, who in 1784 recognized it to be chemically distinct from barytes. It occurs in veins of lead ore at Hexham in Northumberland, Alston in Cumbria, Anglezarke, near Chorley in Lancashire and a few other localities. Witherite is readily altered to barium sulfate by the action of water containing calcium sulfate in solution and crystals are therefore frequently encrusted with barytes. It is the chief source of

barium salts and is mined in considerable amounts in Northumberland. It is used for the preparation of rat poison, in the manufacture of glass and porcelain, and formerly for refining sugar. It is also used for controlling the chromate to sulfate ratio in chromium electroplating baths [1, 6].

Barium carbonate is made commercially from barium sulfide either by treatment with sodium carbonate at 60 to 70°C (soda ash method) or by passing carbon dioxide at 40 to 90°C . In the soda ash process, solid or dissolved sodium carbonate is added to barium sulfide solution, and the barium carbonate precipitate is filtered, washed and dried [2].

The sol-gel techniques offers an excellent control over the stoichiometry, a simple synthesis process, homogeneous particle distribution, good reactivity between components, nano-size particles and allows lower processing temperature.

Recently, Chakrabarti *et al* [3] have patented a technique to synthesize oxide components by auto-combustion of citrate-nitrate gel. Different gel-combustion routes are currently known. These methods are based on gelling of a nitrate solution of the desired metals together with some organic fuel (glycine, citric acid, sucrose, urea, or other water soluble carbohydrates) followed by combustion due to the exothermal redox reaction between nitrate ions and the fuel. This process has the advantage that it can rapidly produce fine and homogeneous powder [4].

The main goals of this work were to prepare nano-crystalline BaCO_3 powders by citrate-nitrate auto-combustion technique and to study the influence of the calcination temperature on the structural variation of barium carbonate powders.

II. EXPERIMENTAL PROCEDURE

In this research, auto gel-combustion technique (a branch of sol-gel method) is used to prepare BaCO_3 nano particle. Gel-combustion method is a wet chemical method. The ingredients used for preparing BaCO_3 nanoparticle consist of barium nitrate, distilled water, nitric acid, citric acid and ammonium hydroxide. The BaCO_3 nanopowder synthesization by the gel-combustion method is summarized in a flow chart shown in Fig. 1.

A. Preparation of sol

Precursor sol of BaCO_3 was prepared by a sol-gel technique. Aqueous solution of the cation (Ba^{2+}) was prepared, dissolving barium nitrate [$\text{Ba}(\text{NO}_3)_2$] in distilled water for solution of Ba^{2+} . The solution of barium prepared as shown above, was added to aqueous solution of citric acid under continuous stirring at $65\text{--}70^\circ\text{C}$ [5]. The required amount of citric acid, for preparing BaCO_3 , was chosen

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corresponding to the molar ratio "citric acid: metal cation = 2.5:1". The main function of citric acid is to provide a polymeric network to hinder cations mobility, which reacts with Ba^{2+} to form metal ion–citric acid complex. Once the CA is dissociated from the Ba^{2+} ions, it will bind to the specific surface of the precipitated $BaCO_3$. Increasing the molar ratio of CA/Ba^{2+} results in more carboxylic group and high pH conditions can enhance the stability constant of metal ion–citric acid and improve the homogeneity[5]. Nitric acid was then added at "citrate/nitrate molar ratio: $CA/NO^{-3} = 1.3$ " and maintaining the pH of the sol at 7, with the addition of ammonium hydroxide. In the gel-combustion method Nitric acid as oxidizer, has important role in combustion step.

B. Preparation of gel

The neutralized solution (sol) was evaporated to dryness by heating at $80\text{ }^{\circ}\text{C}$ - smoothly and steady - on a hot plate with continuous stirring for several hours. As water evaporated, the solution became viscous and finally formed a very viscous brown gel [8].

C. Gel – combustion stage

After the gel obtained, the gel was heated to occur the auto-combustion process. Increasing the temperature up to about $100\text{ }^{\circ}\text{C}$ led to the ignition of the gel[7]. The dried gel burnt in a self-propagating combustion manner until all gels are completely burnt out to form a loose powder[8]. When excessive HNO_3 was added, the combustion was more violent due to the presence of NH_4NO_3 . $BaCO_3$ nanopowder was produced by the citrate-nitrate gel auto-combustion technique. The color of the resultant powder in this stage is black. During the combustion, large amounts of gases such as H_2O , CO , CO_2 and NO are liberated [9].

D. Calcination stage

After auto-combustion of the gel, the produced powders were calcined at three different temperatures ($T = 450, 600$ and $750\text{ }^{\circ}\text{C}$) to obtain the desired single phase powders[9].

E. Characterization

X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used for the characterization of the reaction products. The X-ray diffraction (XRD) patterns of $BaCO_3$ nano-crystals prepared at various calcination temperatures were recorded by the D8 Advanced Bruker system using $CuK\alpha$ ($\lambda = 0.154056\text{ nm}$) radiation with 2θ in the range $10\text{--}65^{\circ}$. Transmission electron microscopy (TEM) of the prepared $BaCO_3$ nanopowders was recorded by the LEO system (model 912 AB) operating at 120 kV . The required sample for TEM analysis was prepared by dispersing the $BaCO_3$ nanopowders in acetone using an ultrasound bath. A drop of this dispersed suspension was put onto 200-mesh carbon-coated Cu grid and then dried in vacuum [10].

III. RESULTS AND DISCUSSION

A. X-Ray Diffraction (XRD)

The phase identification of the as-burnt and calcined powders was performed using X-ray diffraction (XRD). The average crystallite size of the powders was measured by

X-ray line-broadening technique employing the Scherrer formula. The XRD patterns of prepared $BaCO_3$ nanopowders at different calcination temperatures are shown in Figs. 2-5.

It is clear that the powders not calcined (Fig. 2) is crystalline with a bit additional phase. Because of drastic increase of temperature in gel combustion process there are strong picks of orthorhombic structure of $BaCO_3$ in this XRD pattern, without calcination; so in gel-combustion method the calcination temperature is less than the value for the other methods.

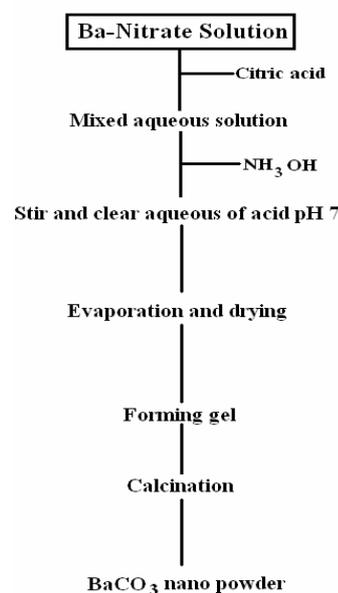


Fig. 1. The flow chart of preparation of $BaCO_3$ by gel-combustion process

Those calcined at $T = 450^{\circ}\text{C}$, 600°C and $750\text{ }^{\circ}\text{C}$ are completely crystallized (Figs. 3, 4 and 5). In this research the calcination started at $T = 450\text{ }^{\circ}\text{C}$ and in this temperature the additional phase falls down, perhaps the elimination occur at less temperature than $T = 450^{\circ}\text{C}$. In addition, the Bragg's peaks of the crystallized powders correspond to each sample agree well with the reflections of pure orthorhombic $BaCO_3$ single phase (witherite) with $a = 5.314\text{ \AA}$ and $b = 8.904\text{ \AA}$. The XRD patterns at all calcination temperatures show that the intensities of three basic peaks of the (111), (021) and (211) planes are more than the other peaks [10].

Table 1 shows the XRD parameters of $BaCO_3$ nano-particle in various crystalline orientations at different calcination temperatures. As seen in Table 1, the width of the strongest peak decreases with increasing of the calcination temperature, which refers to the growth of crystal size and also the intensity of the peaks increase with increasing calcination temperature, which leads to the more crystalline structure[10].

The crystallite size XRD was estimated from the broadening of XRD peaks, using Scherrer's formula (1) [11]:

$$d_{XRD} = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where θ is the Bragg angle of diffraction lines, K is a shape factor taken as 0.9, λ is the wavelength of incident X-rays ($\lambda = 0.154056\text{ nm}$), and β is the full-width at half maximum (FWHM).

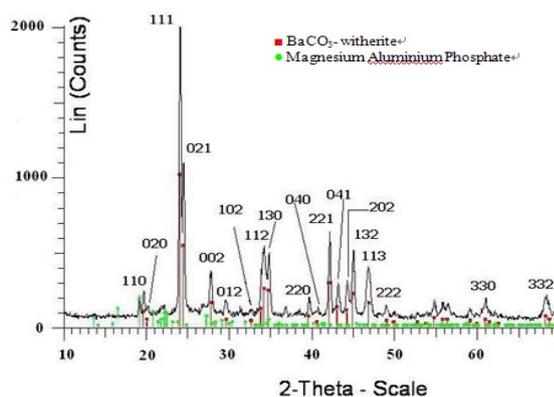


Fig. 2. The XRD patterns of the BaCO₃ nanoparticle before calcination the (with a bit additional phase)

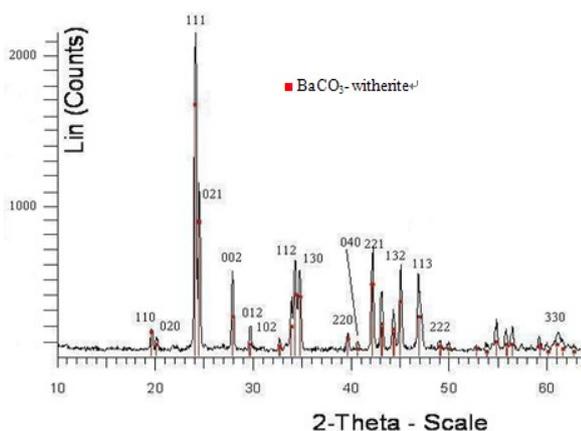


Fig. 3. The XRD patterns of the BaCO₃ nanoparticle calcined at T=450 °C with pure orthorhombic phase of BaCO₃

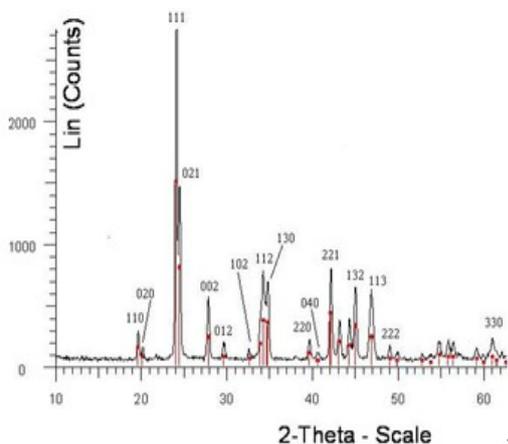


Fig. 4. The XRD patterns of the BaCO₃ nanoparticle calcined at T=600 °C with pure orthorhombic phase of BaCO₃

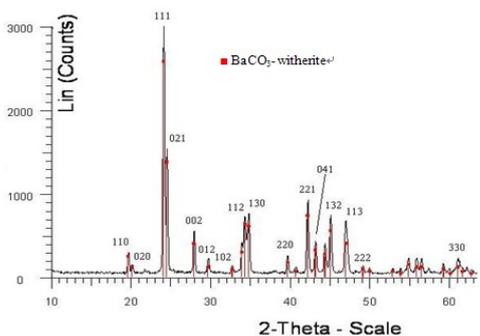


Fig. 5. The XRD patterns of the BaCO₃ nanoparticle calcined at T=750°C with pure orthorhombic phase of BaCO₃

TABLE 1. THE XRD PATTERNS OF PARTICLES IN DIFFERENT CRYSTALLOGRAPHY ORIENTATIONS AT DIFFERENT CALCINATION TEMPERATURES (D (NM) RELATED TO SCHERRER,S FORMULA”)

| hkl | 2θ | d (Å) | Intensity Lin(Cps) | FWHM 2θ (deg) | D (nm) |
|--|-------|-------|--------------------|---------------|--------|
| T = black nanopowder before calcination | | | | | |
| 111 | 24.20 | 3.70 | 2020 | 0.238 | 33 |
| 021 | 24.95 | 3.64 | 1072 | 0.214 | 37 |
| 221 | 42.50 | 2.14 | 627 | 0.272 | 30 |
| T = 450 °C | | | | | |
| 111 | 24.25 | 3.69 | 2180 | 0.237 | 33 |
| 021 | 24.85 | 3.64 | 1325 | 0.206 | 39 |
| 221 | 42.75 | 2.14 | 711 | 0.290 | 29 |
| T = 600 °C | | | | | |
| 111 | 24.25 | 3.69 | 2998 | 0.235 | 34 |
| 021 | 24.85 | 3.64 | 1469 | 0.221 | 36 |
| 221 | 42.60 | 2.14 | 798 | 0.263 | 32 |
| T = 750 °C | | | | | |
| 111 | 24.25 | 3.69 | 3029 | 0.230 | 35 |
| 021 | 25.05 | 3.63 | 1506 | 0.200 | 40 |
| 221 | 42.70 | 2.14 | 922 | 0.273 | 30 |

Table 2 shows the mean crystallite size (<d>) for each calcination temperature by using Scherrer's formula (1).

Fig. 6 shows the variation of mean crystallite size by change of the calcination temperature.

TABLE 2. THE MEAN CRYSTALLITE SIZE IN DIFFERENT ANNEALING TEMPERATURE

| Calcination temperature | <d> |
|-------------------------|---------|
| No calcination | 33.3 nm |
| T = 450 °C | 33.6 nm |
| T = 600 °C | 34 nm |
| T = 750 °C | 35 nm |

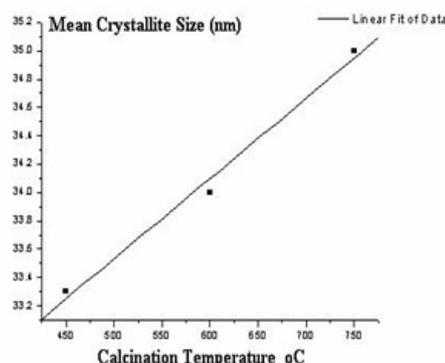


Fig. 6. Variation of mean crystallite size against calcination temperature.

As seen in Table 2 and Fig. 6, the mean crystallite sizes are in the nanometric orders so XRD by using Scherrer's formula (1) confirms that the samples are in nanometric sizes. Scherrer's formula has an accurate result for single crystals while for other kinds of crystals the result is not accurate. Scherrer's formula has this significant advantage that the

crystallite sizes are in the nanometric scale.

In addition, the mean crystallite sizes increase with the increasing of the calcination temperature, which refers to the more crystalline structure.

B. Transmission electron microscopy (TEM)

The TEM micrograph of the BaCO₃ nanopowders calcined at T = 450 °C, T = 600 °C and T = 750 °C are shown in Fig. 7, Fig. 8 and Fig. 9.

The TEM images of the samples -calcined at different temperatures- confirm the nanometric size of the particles in the range of 1-10 nm.

It is clear from the TEM images that the resultant powders are very fine and tiny, so in these sizes (less than 10 nm), it is hard to elaborate the changes between the Fig. 7, Fig. 8 and Fig.9. May be we can say uncertainly the size of the particles increase little by the increase at the calcination temperature.

The TEM images results like XRD (Scherer's formula) results confirm the nanometric sizes of the samples, but TEM shows the sizes in the range of 1 – 10 nm and XRD shows the sizes in the range of 30 nm. This difference in the sizes refers to this fact that: "The TEM shows the size of the particles and XRD shows the size of the crystallites". In addition, the Scherer's formula (1) has good results for single crystals (our samples are not single crystals) and we use Scherer's formula (1) only for confirmation of the nanometric size of the samples before using TEM images.

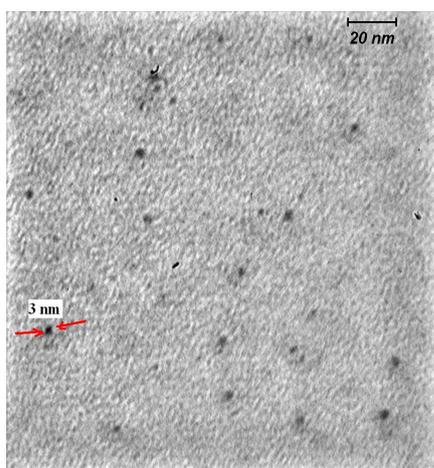


Fig. 7. The TEM image of BaCO₃ nanopowders calcined at 450 °C

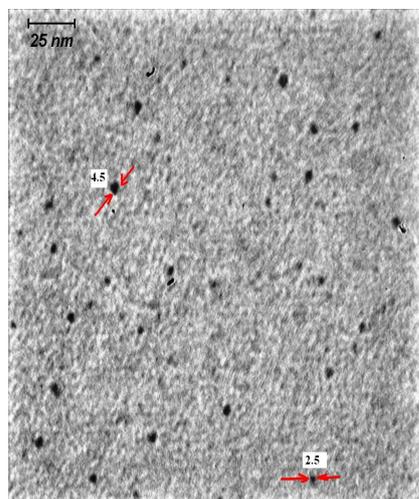


Fig. 8. The TEM image of BaCO₃ nanopowders calcined at 600 °C

IV. CONCLUSIONS

Barium carbonate nanopowders were synthesized successfully by the gel-combustion (sol-gel) method. By using this method the barium carbonate nanoparticle were produced in three different calcination temperatures T = 450 °C, T = 600 °C and 750 °C. The gel-combustion method used in this research as a wet chemical method has many advantages such as excellent control over the stoichiometry, a simple synthesis process, homogeneous particle distribution, good reactivity between components, nano-size particles and lower processing temperature.

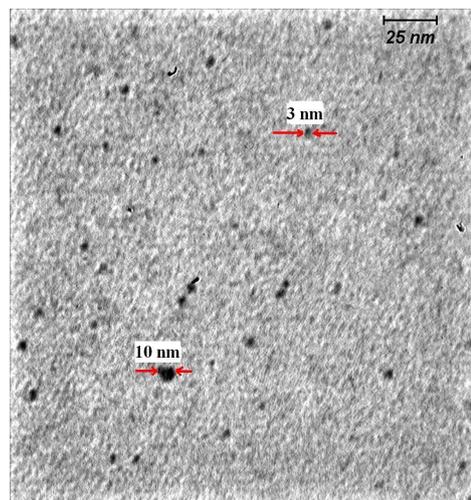


Fig.9. The TEM image of BaCO₃ nanopowders calcined at 750 °C

Nanometric size of the particles were confirmed by the TEM images of the samples that calcined at T = 450 °C, T = 600 °C and T =750 °C. TEM images show that the sizes of the nanoparticles are on the range of 1-10 nm.

Nanometric size of the crystallite was confirmed by XRD with Scherer's formula (1). Scherer's formula predicted the crystallite sizes about 30 nm.

TEM shows the sizes in the range of 1 – 10 nm and XRD shows the sizes in the range of 30 nm. This difference in the sizes refers to this fact that: "The TEM shows the size of the particles and XRD shows the size of the crystallites".

The XRD patterns show that the samples calcined at T = 450, 600 and 750 °C are completely crystallized. The Bragg's peaks of the crystallized powders correspond to each sample agree well with the reflections of pure orthorhombic BaCO₃ single phase (witherite) with a = 5.314 Å and b = 8.904 Å. Despite strong picks of orthorhombic BaCO₃ structure there is an additional phase in the XRD pattern of non-calcined sample. Increase in the calcination temperature decreases the width of the picks, which refers to the growth of crystal size, and also the intensity of the peaks increase with increasing calcination temperature, which means more crystalline structure. XRD by using of Scherer's formula (1) shows that the mean crystallite sizes increase with the increasing of the calcination temperature, which refers to the more crystalline structure.

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