Synthesis of BaCO$_3$ Nanopowder by the Gel-combustion Method at Different Calcination Temperatures and Characterization of the Samples by TEM and XRD

Amir Zelati$^1$, Ahmad Amirabadizadeh$^1$, Ahmad Kompany$^2$, Zobadeh Momeni Larimi$^1$

$^1$Department of Physics, University of Birjand, Iran
$^2$Department of Physics, Ferdowsi University of Mashhad, Iran

Abstract. Barium carbonate nanopowder with composition BaCO$_3$ (Witherite) was prepared in this research. The gel-combustion method was applied to reach the required result. 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 $\leq 400^\circ$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 $T = 450^\circ$C, $T = 600^\circ$C and $750^\circ$C. The pure orthorhombic phase was found at $450^\circ$C. The effect of calcination temperature was studied in three various temperatures. The size of particles were produced by this method are between 1nm to 10nm. TEM and XRD were used for characterization of the samples.

Keywords: barium carbonate, Witherite, nanopowder, gel-combustion method, TEM, XRD

1. Introduction

Barium carbonate (BaCO$_3$), also known as Witherite, is a chemical compound used in rat poison, bricks, ceramic glazes and cement. 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.

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].

Barium carbonate is made commercially from barium sulfide either by treatment with sodium carbonate at 60 to 70 $^\circ$C (soda ash method) or by passing carbon dioxide at 40 to 90 $^\circ$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.

The main goals of this work were to prepare nano-crystalline BaCO₃ powders by citrate-nitrate auto-combustion technique and to study the influence of the calcination temperature on the structural variation of barium carbonate powders.

2. Experimental procedure

BaCO₃ nanopowder synthesization by the gel-combustion method is summarized in a flow chart shown in Fig. 1. Precursor sol of BaCO₃ was prepared by a sol-gel technique. Aqueous solution of the cation (Ba²⁺) was prepared, dissolving barium nitrate [Ba(NO₃)₂] in distilled water for solution of Ba²⁺. The solution of barium prepared as shown above, was added to aqueous solution of citric acid under continuous stirring at 65-70 °C [6]. The required amount of citric acid, for preparing BaCO₃, was chosen corresponding to the molar ratio citric acid: metal cation = 2.5:1. Nitric acid was then added as oxidizer at citrate/nitrate molar ratio: CA/NO₃⁻ =1.3 and maintaining the pH of the sol at 7 with the addition of ammonium hydroxide. The sol of BaCO₃ was heated at about 80 °C to evaporate all of the water and to obtain the gel. BaCO₃ powder was produced by the citrate-nitrate gel auto-combustion technique. When excessive HNO₃ was added, the combustion was more violent due to the presence of NH₄NO₃. The colour of the resultant powder in this stage is black. After auto-combustion of the gels, the produced powders were calcined at different temperatures to obtain the desired single phase powders.

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 BaCO₃ nano-crystals prepared at various calcination temperatures were recorded by the D8 Advanced Brucker system using CuKα (λ = 0.154056 nm) radiation with 2θ in the range 10-80°. Transmission electron microscopy (TEM) of the prepared BaCO₃ 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 BaCO₃ 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.

![Fig. 1: The flow chart of preparation of BaCO₃ by gel-combustion process](image)

3. Results and discussion

The XRD patterns of prepared BaCO₃ nanopowders at different calcination temperatures are shown in Fig. 2(a)-(d).
Fig. 2: The XRD patterns of the BaCO$_3$ nano-particles calcined at different temperatures, (a) the nano-powder produced before calcination (with a bit additional phase), (b) calcination at 450 °C with pure orthorhombic phase of BaCO$_3$, (c) calcination at 600 °C with pure orthorhombic phase of BaCO$_3$, (d) calcination at 750 °C with pure orthorhombic phase of BaCO$_3$.

It is clear that the powders not calcined (Fig. 2(a)) 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$_3$. 

148
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. Those calcined at $T = 450$, 600 and 750 °C are completely
crystallized (Fig. 2(b), (c) and (d)). In this research the calcination started at $T = 450$ °C and in this
temperature the additional phase falls down, perhaps the elimination occur at less temperature than $T = 450$ °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 $a = 5.314$ Å and $b = 8.904$ Å. 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.

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 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.

The TEM micrograph of the BaCO$_3$ nanopowders calcined at 750 °C is shown in Fig. 3. The TEM image
confirms the nanometric size of the particles in the range of 1-10 nm.

Table 1 The XRD patterns of particles in different crystallography orientations at different calcination temperatures

<table>
<thead>
<tr>
<th>hkl</th>
<th>$2	heta$</th>
<th>d (Å)</th>
<th>Intensity (Lm(Cps))</th>
<th>FWHM $2	heta$ (deg)</th>
<th>Identification with (hkl) value</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>24.20</td>
<td>3.70</td>
<td>2020</td>
<td>0.238</td>
<td>Orthorhombic BaCO$_3$</td>
</tr>
<tr>
<td>021</td>
<td>24.85</td>
<td>3.64</td>
<td>1072</td>
<td>0.214</td>
<td>Orthorhombic BaCO$_3$</td>
</tr>
<tr>
<td>221</td>
<td>42.70</td>
<td>2.14</td>
<td>627</td>
<td>0.272</td>
<td>Orthorhombic BaCO$_3$</td>
</tr>
<tr>
<td>T = 450 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>111</td>
<td>24.25</td>
<td>3.69</td>
<td>2180</td>
<td>0.237</td>
<td>Orthorhombic BaCO$_3$</td>
</tr>
<tr>
<td>021</td>
<td>24.85</td>
<td>3.64</td>
<td>1323</td>
<td>0.206</td>
<td>Orthorhombic BaCO$_3$</td>
</tr>
<tr>
<td>221</td>
<td>42.75</td>
<td>2.14</td>
<td>711</td>
<td>0.290</td>
<td>Orthorhombic BaCO$_3$</td>
</tr>
<tr>
<td>T = 600 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>111</td>
<td>24.25</td>
<td>3.69</td>
<td>2998</td>
<td>0.235</td>
<td>Orthorhombic BaCO$_3$</td>
</tr>
<tr>
<td>021</td>
<td>24.85</td>
<td>3.64</td>
<td>1469</td>
<td>0.221</td>
<td>Orthorhombic BaCO$_3$</td>
</tr>
<tr>
<td>221</td>
<td>42.80</td>
<td>2.14</td>
<td>788</td>
<td>0.304</td>
<td>Orthorhombic BaCO$_3$</td>
</tr>
<tr>
<td>T = 750 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>111</td>
<td>24.25</td>
<td>3.69</td>
<td>3029</td>
<td>0.230</td>
<td>Orthorhombic BaCO$_3$</td>
</tr>
<tr>
<td>021</td>
<td>25.05</td>
<td>3.63</td>
<td>1506</td>
<td>0.200</td>
<td>Orthorhombic BaCO$_3$</td>
</tr>
<tr>
<td>221</td>
<td>42.70</td>
<td>2.14</td>
<td>922</td>
<td>0.273</td>
<td>Orthorhombic BaCO$_3$</td>
</tr>
</tbody>
</table>

Fig. 3: The TEM image of BaCO$_3$ nanopowders calcined at 750 °C

4. Conclusions
Barium carbonate nanopowders were synthesized successfully by the gel-combustion (sol-gel) method. By using this method the barium carbonate nano-particles were produced in three different calcination temperatures $T = 450 \, ^\circ C$, $T = 600 \, ^\circ C$ and $750 \, ^\circ C$. The gel-combustion method used in this research 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. Nanometric size of the particles were confirmed by the TEM image of the sample that calcined at $750 \, ^\circ C$ and the size of the nano-particles are on the range of 1-10 nm. The XRD patterns show that the samples calcined at $T = 450$, 600 and 750 $^\circ C$ are completely crystallized. 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 $a = 5.314 \, \AA$ and $b = 8.904 \, \AA$. Despite strong picks of orthorhombic BaCO$_3$ 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.

5. References