December 2009 *Volume 3 Issue 2*

Trade Science Inc.

Nano Science and Nano Technology

An Indian Journal

Short Communication

NSNTAIJ, 3(2), 2009 [58-60]

Preparation and mechanism of nano-$BaZrO_3$ by solid-state reaction at low temperature

Ding Shi-Wen*, Zhang Yuan-Yuan, Zhang Hong-Jun

College of Chemistry and Environmental Science, Hebei University, Baoding Hebei 071002, (P. R. CHINA)

E-mail : dingsw-hbu@163.com

Received: 25th August, 2009 ; Accepted: 4th September, 2009

ABSTRACT

Nano-$BaZrO_3$ was synthesized by Solid-State Reaction at Low temperature, useing Ba (OH) $_2$ • $8H_2O$ and $ZrOCl_2$ • $8H_2O$ as raw materials. First, hydrolysis $ZrOCl_2$ • $8H_2O$ preparation of high-activity ZrO_2 • H_2O (H_2ZrO_3) then evenly grinding after mixtured with Ba (OH) $_2$ • $8H_2O$ by 1:1 (mol), finally Drying at 100 °C reaction obtained a cubic barium zirconic nanometer crystal. TEM photograph showed that they were uniform and substantially quadrate particles with the size of 40~80nm. The experiment Determined that the chemical reaction is rate controlling step at low temperature solid state reaction.

KEYWORDS

Low-temperature solid-state reaction;
Nano barium zirconate;
Preparation process.

INTRODUCTION

$BaZrO_3$ ceramics is one of the most important electronic ceramic materials. Under high temperatures it exhibited good ionic conductivity when zirconium was partly replaced by different price metallic ion. Because of its excellent chemical stability and mechanical strength, it is a kind of promising solid electrolyte materials.[1] $BaZrO_3$ catalyst has a good performance of storage nitrogen and sulfur resistance[2]. Therefore the synthetic method of $BaZrO_3$ always is the domestic and foreign material research focus[3-6]. Synthesis by solid state reaction is a cheap and simple preparation method, with the simple process, high yield, the reaction conditions is easy to contral, without solvents, and less pollution.[7] However, traditional solid-state reaction needs high temperature up to 1350 °C, and not only high energy consumption, but also easily particles sintered, which made the powder heavy agglomeration and poor surface activity . Considering that, in our present work, a new method called solid-state reaction at low temperature has been explored to synthesize $BaZrO_3$. This method has many advantages, such as no solvents, little pollution and high productive.

EXPERIMENTAL

Chemicals and instruments

Y-2000 X-ray Diffractometer (Dandong), JEM-100SX Transmission Electrical Microscope (Japan), QM-3SP2 planetary ball mill (Nanjing) DHG-9076A blast type electric oven thermostat (Shanghai) etc

$Ba(OH)_2 \cdot 8H_2O$ $ZrOCl_2 \cdot 8H_2O$ are analytical reagents made in China. All experiments were carried out in the deionized water.

Synthesis of $BaZrO_3$ powder

That a certain amount of $ZrOCl_2$ • $8H_2O$, adding

Short Communication

few 1:1 HCl, dissolved in 100 mL water for hydrolysis. The pH value of the solution was adjusted to 7~8 by dropping 1:1 $NH_3 \cdot H_2O$. Then it was filtered and washed with deionized water until the Cl^- could not be detected. Subsequently it was mixed with needed $Ba(OH)_2 \cdot 8H_2O$(molar ratio is Ti:Ba=1:1). The mixture was milled for 60 min at room temperature, then dried at 100 °C for 15h.

RESULTS AND DISCUSSION

XRD analysis of $BaZrO_3$ powder

Comparing XRD pattern of synthetical $BaZrO_3$ powder with JCPDS Card（06-0399), to demonstrate that that synthetical $BaZrO_3$ powder is pure cubic phase. (shown in Figure 1)

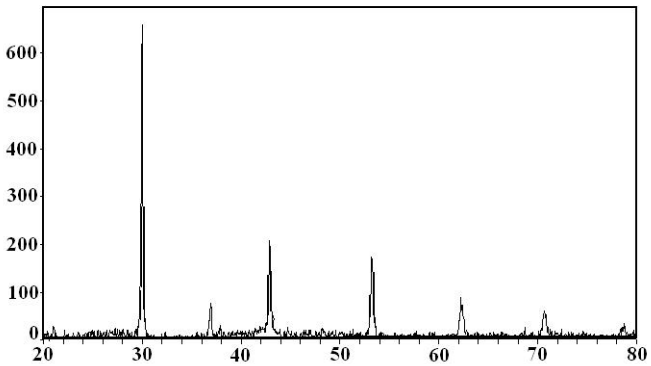

Figure 1 : XRD pattern of synthetical $BaZrO_3$

TEM analysis of $BaZrO_3$ powder

TEM photograph of the powder shows that the particles are uniform and substantially quadrate particles with the size of 40~80nm in diameter.(shown in Figure 2)

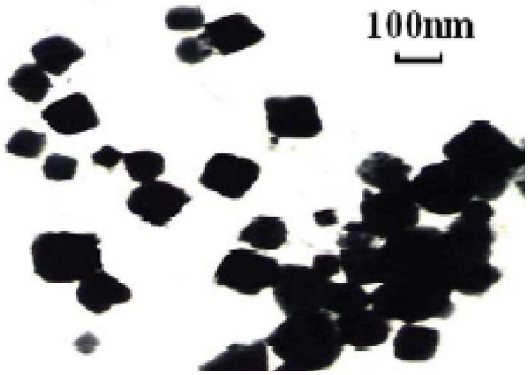

Figure 2 : TEM photograph of sample

Influence of reaction temperature

The mixture was devided into six parts, then dried respectively at room temperature, 40°C, 60°C, 80°C, 100°C and 120°C for 12D, 75h, 48h, 24h, 15h and12h in order to be dried completely. XRD patterns of the dried powder are shown in Figure 3.

In Figure 3: 1, 2, 3, 4, 5, 6 respectively is the XRD pattern of dried powder at room temperature, 40 °C, 60 °C, 80 °C, 100 C and 120 °C.

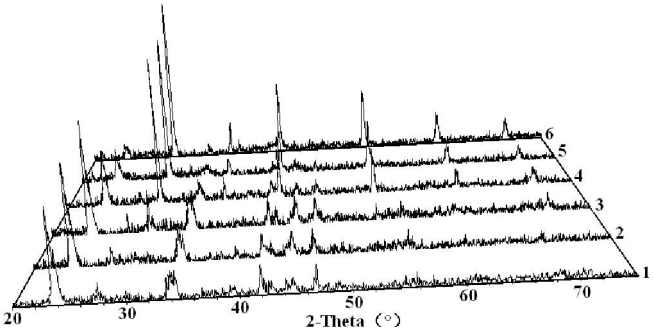

Figure 3 : XRD patterns of powders dried at different temperatures

It is can be seen that dried powder both at room temperature and 40°C are the $BaCO_3$ characteristic diffraction peak. As temperature rising, 60°C starts to appear $BaZrO_3$ diffraction peak, 80°C has been completely appeared $BaZrO_3$ characteristic diffraction peak. But still have the obvious $BaCO_3$ impurity peak. 100°C $BaCO_3$ reduces to the minimum.

So we confiemed the optimal reaction temperature is 100°C.

Influence of reaction time

In order to determine how long the mixture needs to form $BaZrO_3$ at 100°C, the mixture react respectively for 3h, 4h, 5h, 6h, 9h, 12h, 15h under 100°C, and then dried at room temperature. Their XRD pattrerns are shown in Figure 4.

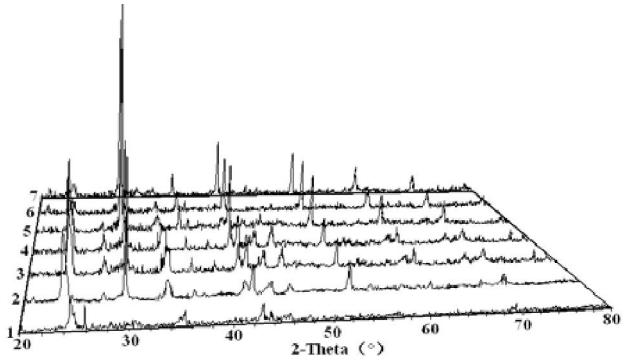

Figure 4 : XRD patterns of sample reacting different time under 100°C

Short Communication

In Figure 4: 1, 2, 3, 4, 5, 6, 7 respectively indicates XRD pattern of powders reacting for 3h, 4h, 5h, 6h, 9h, 12h, 15h under 100 °C, then dried at room temperature .

It can be seen that when the reaction time is 3h, only has $Ba(OH)_2$ and the $BaCO_3$ diffraction peak, no $BaZrO_3$ occures. When the reaction time is 4h, $BaZrO_3$ phase starts to form. And $Ba(OH)_2$ phase disappeared, but still had the massive $BaCO_3$ existence. The intensity of $BaZrO_3$ diffraction peaks increases with the reaction time, while that of $BaCO_3$ gradually decrease.

Reaction mechanism

Diffusion, reaction, nucleation and growth are the four steps of the solid-state reaction. In the past, diffusion or nucleation is considered to be the rate-determining step of the high temperature solid-state reaction. However, in the low temperature solid-state reaction, the four steps may become rate-determining step. From Figure 3, it can be seen that the strength of the $Ba(OH)_2$ diffraction peaks is very small from the start to the end, so we can know the diffusion from $Ba(OH)_2$ to H_2ZrO_3 is very quickly. In Figure 3, reaction under 100°C just exhibits the $BaZrO_3$ diffraction peaks and in Figure 4, reaction for 4 h under 100 just begins to exhibit the $BaZrO_3$ diffraction peaks with high strength. From the above, we draw a conclusion that diffusion, nucleation and growth is quick. So we confiem that reaction is the rate-determining step of the solid-state reaction at low temperature.

In addition, as a result of the precursors of this reaction is fresh prepared and very lively H_2ZrO_3 ($ZrO_2 \cdot xH_2O$)[8], which has small particle size, high activity is extremely easy reacted with $Ba(OH)_2$, so make the reaction at lower temperatures can be achieved.

4. CONCLUSIONS

(1) It is first time to use solid-state reaction at low temperature to synthesize cubic $BaZrO_3$. The method is high productive and partly process achieving economic atom reaction according to the ideas of green chemistry.

(2) In the solid-state reaction at low temperature, chemical reaction is the rate-determining step.

ACKNOWLEGEMENTS

This work was supported by the Natural Science Foundation of Hebei Province, China (Grant No. B2008000574)

REFERENCES

[1] Zheng Wen-Jun, Meng Xian-Ping, Zhou Feng-Qi, et al.; Chemical Journal of Chinese Universities., **17(11)**, 1666-1669 **(1996)**.

[2] Gao Ai-Mei, Wang Zhou-Feng; Journal of South China University of Technology., **36(17)**, 134-137 **(2008)**.

[3] F. Boschini, A.Rulmont, R.Cloots, et al.; Journal of the European Ceramic Society, **29(8)**, 1457-1462 **(2009)**.

[4] Lu Zhou-Guang, Tang You-Gen, Chen Li-Miao, et al.; Journal of Crystal Growth, **266(4)**, 539-544 **(2004)**.

[5] M.M.Bu´cko, J.Obłąkowski; Journal of the European Ceramic Society, **27(13-15)**, 3625-3628 **(2007)**.

[6] A.Aimable, B.Xin, N.Millot, et al.; Journal of Solid State Chemistry, **181(1)**, 183-189 **(2008)**.

[7] Lian Hong-fang; Guang dong Chemical, **7(33)**, 8-10 **(2006)**.

[8] Huang Yue-Xiang, Guo Cun-Ji; Journal of Inorganic Materials, **7(4)**, 483-486 **(1992)**.