UNIVERSITI PUTRA MALAYSIA

# SYNTHESIS AND MORPHOLOGY OF HIGH DENSITY BARIUM ZIRCONATE CERAMICS

SELVARAJAN SUBRAMANIAM

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# SYNTHESIS AND MORPHOLOGY OF HIGH DENSITY BARIUM ZIRCONATE CERAMICS



**By**

**SELVARAJAN SUBRAMANIAM**

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**Chairman : Associate Professor Dr Mansor Hashim**

**Faculty : Institute of Advance Technology**

Barium Zirconate ($BaZrO_3$) is an inert target material with high resistance to temperature and chemical reaction, which can be used as a crucible. In some literatures, $BaZrO_3$ with small particle size is also proposed as material for multilayer capacitors. In this research high dense $BaZrO_3$ has been synthesized through a common method, solid-state reaction, where large amount of fine $BaZrO_3$ powder can be obtained and further sintered at high temperature to gain high density material.

In this study, nitrate precursors were used to lower the formation temperature of $BaZrO_3$. The raw materials ($Ba(NO_3)_2$ and $ZrO(NO_3)_2.H_2O$ in 1:1 molar ratio) were calcined at $800^0C$ for 8h to obtain a fine and pure $BaZrO_3$ crystal. The calcine powder was analysed with X-ray diffraction to confirm that there were no unwanted impurities. The calcined powder was also analysed with laser particle-size analyser and scanning electron microscope to gain more information on the particle sizes and morphology. The

low temperature of calcination produced fine powder (< 1μm). Fine powders always facilitate fast boundary diffusion during sintering.

Sintering the green pellet between $1200^0C$ and $1700^0C$ showed vast information of morphology changes. $BaZrO_3$ with 0.6μm was obtained at $1200^0C$ with dwell time of 24h. Further sintering at $1600^0C$ for 6h produced a high dense pellet with no or near zero porosity and about 90% density compared to theoretical value. The crystallite size is ranged between 0.36μm to 0.44μm. However, the pellets had shrink of about 13%.

To prevent the large shrinkage, sintering aids were used. Magnesium oxide (MgO), Yttrium oxide ($Y_2O_3$), Aluminium oxide ($Al_2O_3$), and Barium Stannum oxide ($BaSnO_3$) were added up to 5% separately with the calcined $BaZrO_3$ powder and sintered between $1500^0C$ and $1700^0C$. Interestingly, with the presence of MgO, $Y_2O_3$ and $Al_2O_3$ the sintering shrinkage was reduced to only 2%. Even though there was some level of porosity, $BaZrO_3$ with MgO and $Y_2O_3$ pellets with shown about 90% densification.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia bagi memenuhi keperluan Ijazah Master Sains

**SINTESIS DAN MORFOLOGI BARIUM ZIRCONATE DENGAN KETUMPATAN TINGGI**

**Oleh**

**SELVARAJAN SUBRAMANIAM**

**Ogos 2001**

**Pengerusi : Professor Madya Dr. Mansor Hashim**

**Fakulti : Institut Teknologi Maju**

Bariun Zirconate ($BaZrO_3$) adalah sejenis bahan sasaran lengai yang mempunyai ketahanan yang tinggi terhadap suhu dan tindakbalas kimia. $BaZrO_3$ boleh digunakan sebagai bekas untuk memanaskan bahan lain pada suhu yang tinggi. Mengikut kajian, $BaZrO_3$ yang mempunyai saiz partikel yang kecil boleh digunakan sebagai penebat untuk kapasitor berlapis. Dalam kajian ini, $BaZrO_3$ yang berketumpatan tinggi telah dihasilkan secara tindak balas keadaan pepejal bagi menghasilkan serbuk $BaZrO_3$ yang halus dan memberikan bahan ketumpatan tinggi apabila disinter pada suhu tinggi.

Dalam kajian ini, sebatian nitrat digunakan sebagai bahan asas (bukan sebatian oksida atau karbonat, yang biasa digunakan) untuk mengurangkan suhu tindakbalas pembentukkan $BaZrO_3$. Bahan-bahan tindakbalas ($Ba(NO_3)_2$ and $ZrO(NO_3)_2.H_2O$ dalam kuantiti 1:1molar) telah dipanaskan bersama-sama pada suhu $800^0C$ selama 8 jam untuk mendapatkan $BaZrO_3$ yang tulen dan yang mempuyai saiz hablur yang kecil. Hasilnya telah dianalisis dengan alat X-ray untuk menentukan ketulenannya. Hasilnya juga telah dianalisis dengan 'laser particle size analyser' dan mikroskop elektron untuk mendapat maklumat yang lebih mendalam mengenai saiz dan morfologinya. Suhu tindakbalas yang rendah telah menghasilkan saiz butir hasil tindakbalas yang kecil (< 1μm). Saiz butir yang yang kecil dapat mempercepatkan tindakbalas antara partikal-partikal $BaZrO_3$ semasa pensinteran.

Seterusnya, pelet dibentuk dari hasil tindakbalas di atas dan disinterkan antara suhu $1200^0C$ dan $1700^0C$. Julat suhu yang besar dapat memberi maklumat yang jelas mengenai perubahan morfologi. $BaZrO_3$ yang dipanaskan pada suhu $1200^0C$ selama 12 jam mempunyai partikel bersaiz 0.6μm. Pemanasan yang seterusnya pada $1600^0C$ selama 6 jam telah menghasilkan $BaZrO_3$ yang hampir tidak ada keliangan serta mempunyai ketumpatan hampir 90% berbanding dengan nilai teori. Saiz kristal $BaZrO_3$ berjulat antara 0.36μm to 0.44μm. Walau bagaimanapun, pelet yang dihasilkan ini telah mengalami pengecutanan yang besar iaitu sebanyak lebih dari 13%.

Untuk mengurangkan pengecutan ini, bahan yang membantu pensinteran (sintering aid) telah digunakan. Magnesium oksida, Yttrium oksida, Aluminium oksida and Barium Stannum oksida ditambah sehingga 5% secara berasingan kepada $BaZrO_3$ dan dipanaskan antara suhu $1500^0C$ dan $1700^0C$. Dengan kehadiran Magnesium oxida, Yttrium oxida dan Aluminium oxida dapat mencegah pengecutan. Pengecutan yang berlaku hanya sebanyak 2% sahaja. Walaupun, mempunyai sedikit sebanyak keliangan $BaZrO_3$ dangan Magnesium oksida dan Yttrium oksida telah menghasilkan pelet yang mempunyai ketumpatan hampir 90%.

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I certify that an Examination Committee meet on 23rd August 2001 to conduct the final examination of Selvarajan Subramaniam on his Master of Science thesis entitle "Synthesis and Morphology of High Density Barium Zirconate ceramics" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

MOHD. SAPUAN SALIT, Ph.D, P.Eng.
Faculty of Engineering,
Universiti Putra Malaysia.
(Chairman)

MANSOR HASHIM, Ph.D
Associate Professor,
Institute of Advance Technology
Universiti Putra Malaysia.
(Member)

TENG WAN DUNG, Ph.D
Senior Researcher
SIRIM Sdn. Bhd.
Malaysia
(Member)

AZMI ZAKARIA, Ph.D
Faculty of Science and Environmental Studies
Universiti Putra Malaysia.
(Member)

ZAINAL ABIDIN SULAIMAN
Associate Professor,
Faculty of Science and Environmental Studies
Universiti Putra Malaysia.
(Member)

MOHD. GHAZALI MOHAYIDIN, Ph.D.
Professor/Deputy Dean of Graduate School
Universiti Putra Malaysia.

Date: 10 DEC 2001

This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirement for the degree of Master of Science.

AINI IDERIS, Ph.D.
Professor
Dean of Graduate School,
Universiti Putra Malaysia

Date : 10 JAN 2002

I hereby declare that the thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

**SELVARAJAN SUBRAMANIAM**

**Date** : 9/11/01

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# NOMENCLATURE

| | |
|---|---|
| $\theta$ | angle |
| $\rho$ | density |
| $\lambda$ | wavelength |
| μm | micrometer |
| °C | temperature in Celsius |
| Å | $10^{-10}$m |
| a, b, c | crystal edges |
| BBC | central ion |
| d-spacing | interplanar spacing |
| DTA | Differential Thermal Analysis |
| FCC | face central ion |
| Ghz | Gigahezt |
| h, k, l | Miller indices |
| JCPDS | Joint Committee for Powder Diffraction Standards |
| K | Kelvin |
| Kgf | kilogram force |
| La | Lanthanum |
| m | mass |
| P | pressure |
| Pa | Pascal |

| | |
|---|---|
| Pb | Plumbum |
| ppm | part permillion |
| PVA | Polyvinyl alcohol |
| Q | dielectric quality factor |
| SEM | Scanning Electron Microscope |
| Sn | Stanum |
| Sr | Stronium |
| SSR | Solid-state reaction |
| TCK | Temperature coefficient of dielectric constant |
| TG | Thermogravitmetry |
| V | volume |
| wt | weight |
| XRD | X-ray diffraction |

# CHAPTER I

# INTRODUCTION

## History of Ceramics

Hand mixing, hand building, scratch and slip decorating of earthenware can be backdated to even before 5000 B.C. Since then the use of ceramics has been growing slowly with time. Shaping by processed material in slip cast mould and firing in a close kiln was subsequently developed. In the 18$^{th}$ and 19$^{th}$ centuries, the use of ceramic materials became more important due to its stability and capability to withstand thermal resistance. With the development of new and sophicated equipment such as X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) in the 20$^{th}$ century, material systems have become more refined, and special compounds were developed, synthesised and fabricated into the products used for refractory and electronic applications (James, 1998).

## Relevance, Importance and Application of Ceramics

Ceramic materials are polycrystalline inorganic materials which consist of metallic and/or non-metallic elements bound together primarily by ionic and/or covalent bonds. The chemical composition of ceramic materials varies considerably, from simple compound to mixture of many complex phases bonded together. The properties of ceramics are also varying due to their bonding characteristics. The wide range of materials that are known as ceramics includes most of the natural minerals of the earth such as the silicates, oxides, carbonates, sulphides, as well as glasses and glass ceramics. These ceramic materials have relatively high melting temperatures and high chemical stability in many hostile environments due to the stability of their strong bonds. These materials also are typically insulative to the passage of electricity and heat due to the absence of conductive electron(s).

In general, ceramics materials used for engineering applications can be divided into two groups. Firstly the traditional ceramics made from three basic compounds clay, silica ($SiO_2$), and feldspar ($K_2OAl_2O_3.6SiO_2$), such as porcelain. Secondly the engineering ceramics which are pure or nearly pure compounds, such as, alumina ($Al_2O_3$), silicon carbide (SiC), silicon nitride ($Si_3N_4$) and zirconia ($ZrO_2$) etc (William and Rainforth, 1994).

Advanced ceramics are further classified into two groups, viz., structural and electronic ceramics. The study of advanced ceramic materials such as electronic ceramics involves many disciplines including chemistry, physics, metallurgy, mechanical engineering and materials science.

Electronic ceramics originally were used only as electrical insulators. However, depending on their composition and the fabrication cycle used, current electronic ceramics exhibit a wider range of properties (that is, their polarisation, mechanical, and optical responses) which may be controlled through composition control, chemical substitution, doping, and fabrication conditions, and in some cases due to the unique inherent characteristics.

To understand the behaviour of ceramics, the need to understand the relationship between the observed material properties and the underlying physical phenomena responsible for those properties is warranted. For example, the presence of oxygen vacancy point defects in $ZrO_2$ ceramics leads to their use as oxygen sensor in automotive and other applications. Different applications of ceramics depend on material structural features from the atomic to the macrostructural level. Features such as atomic arrangement (crystal structure), point defects, domain structure, and microstructure are defined to the observed electronic properties of the material.

Chemical synthesis occupies a central position in advanced ceramics development because the experimental methods allow control of properties. Electronic ceramics such as $BaTiO_3$ and $SrTiO_3$ are used as capacitors, $SnO_2$ and $ZrO_2$ are used as gas sensors, and (Mn,Zn) $Fe_2O_4$ is used as a magnet. Some electronic ceramics are used as superconductors, varistors and piezoelectrics (Segal, 1989). The electronic ceramic market shown in Figure 1.1 indicates that the maximum percentage goes to cutting tools industry (24%) and follows by electronic (integrated circuit) industry (21%). The third industrial application of electronic ceramics is devoted to capacitor industry (18%). (Iftetan, 1999)

Ceramics technology consists of initial densification and sintering of the raw powder so that the phase and crystalline structures and the microstructure of the final product satisfy the given requirement. The raw materials may be either simple compounds (e.g. oxides) of metals or more complex compounds that, during the fabrication process, decompose to form simple oxides. In order to ensure desired phase composition of the powder mixture, the materials are subjected to thermal treatment such as calcination. In the case of non-oxides, such as silicon carbide, silicon nitride and aluminium nitride, the processing requires a special environment and equipment.

### General Introduction of Alkaline-Earth Zirconates

The double oxides of general formula $MBO_3$ formed between the oxides of alkaline- earth metals (M= Ca, Sr, Ba and Mg) and those of some group IV elements. These oxides are of great importance to industrial and technological application. For instance, the alkaline–earth carbonates are the well known precursors to innumerable inorganic and ceramics syntheses and reaction, while alkaline--earth silicates are of relevance and direct bearing in the slag chemistry of industrial production of iron and steels. Similarly, the discovery of superconductivity in 'copper-free' cubic perovskite systems such as $BaPb_{1-x}Sb_xO_3$ (Tc = 3.5 K at x = 0.25) and $BaPb_{2\ 1-x}Ba_xO_3$ (Tc = 13 K at x = 0.3) has triggered much activity in the pseudobinary alkaline earth oxide-$PbO(O_2)$ system (Iftetan, 1999). In addition, the technological impact of closely structure-related titanates ($MTiO_3$) of the alkaline-earth metals is too great to be overlooked, of which Sr, Ba and Mg titanntes are the most important electroceramics.

The alkaline-earth zirconates having the general chemical formula $MZrO_3$ · ($M$= Ca, Sr and Ba) with perovskite structure, have been projected as potential structural and electronic ceramics. In suitable doped forms they have been claimed to become ionic and/or electronic conductors. Corresponding titanates, $BaTiO_3$ and $SrTiO_3$ are well-known electroceramic material and commercially produced as low dielectric constant, high resistance and low TCK (temperature coefficient of dielectric constant) components. However, there is a lack of reliable technical information on the $BaZrO_3$ system in the published literature. Most of the available literature is limited to the procedure to produce fine $BaZrO_3$ powder through various sintering methods.

## The Objective of Work

In view of the importance of $BaZrO_3$ system as potential ceramics for applications such as:

- Inert substrate for thin film deposition
- Structural material such as crucibles for reaction, melting and sintering experiments of oxides and non-oxides, and

the information gaps in the reported research, this study was taken up. This investigation was to study the systematic trend in the properties of the resulting ceramic powder and dense pellets. Synthesis of $BaZrO_3$ in phase pure form has been carried out by conventional yet modified solid-state reaction (SSR). The objective