Synthesis, Thermal Behaviour and Structure of Barium Zirconate from an Oxalate Method

Mukhlis M. Ismail*, Abdulkareem Z. Khalf *, and Abdulrahman K. Ali *

* University of Technology / School of Applied Sciences.

Abstract

Barium Zirconate BaZrO$_3$ fine powders were prepared by oxalate method using BaCl$_2$.2H$_2$O, TiCl$_4$ and oxalic acid as starting materials. The precursor (BaZrO(C$_2$O$_4$)$_2$.xH$_2$O) has been synthesized and characterized by combination of spectroscopic and thermal analysis. The precursor under goes thermal decomposition, in two major steps: dehydration to give anhydrous barium zirconyle oxalate and decomposition to produce BaZrO$_3$ fine powders. BaZrO$_3$ started to crystalline phase at 600°C and became a pure phase at 800°C according to FTIR and XRD results.

Introduction

Barium zirconate is an interesting materials for refractory applications as well as a good substrate for the manufacturing of high temperature superconductors[1]. The conventional processing of ceramic powders formation such as BaTiO$_3$ or BaZrO$_3$ involves mixing oxides and / or carbonate using a ball mill and the calcinations of the resulting mixture at an appropriate temperature usually higher than 1000°C[2]. The conventional method of synthesizing BaZrO$_3$ is the solid state reaction method, which involves repeating milling and calcinations (>1200°C) of BaCO$_3$ and ZrO$_2$ powders. This method is suitable for large processing of these electroceramics, the process
has inherent disadvantages including inhomogeneous mixing, impurities introduced during milling, broad particle size distribution, incomplete carbonate burn out during calcinations and formation of non-eqiumolar barium zirconate, such as Ba$_2$ZrO$_4$, BaZr$_2$O$_5$ and BaTi$_4$O$_9$[3]. Recently, wet chemical technologies such as sol-gel method[4], alkoside synthesis[5] and the hydrothermal method[6, 7] have replaced the classical solid state reaction for the preparing of BaZrO$_3$.

In the present work, we prepared barium zirconyle oxalate using ZrOCl$_2$.8H$_2$O, BaCl$_2$.2H$_2$O and C$_2$H$_2$O$_4$.2H$_2$O solution, and then BaZrO$_3$ are formed after annealing it at a definite temperature.

### Experimental

The precipitate BaZrO(C$_2$O$_4$)$_2$.xH$_2$O was obtained by titration of barium chloride and zirconyle chloride solutions by an oxalic acid solution. The conditions to obtain a pure compound were as follows: 1 mole from ZrOCl$_2$.8H$_2$O (purity 99%) and 1 mole from BaCl$_2$.2H$_2$O (purity 99%) were dissolved at a room temperature. This solution was heated at 80°C and slowly titration under constant stirring by 3 moles oxalic acid dried at room temperature. The chemical formula was confirmed from thermo gravimetric analysis, FTIR spectroscopy and XRD.

### Results

The XRD patterns of the prepared and calcined powder at 400°C and 800°C are demonstrated in Fig. 1a b and c respectively. No BaZrO$_3$ characteristic diffraction peaks could be discerned at 250°C and 400°C as
shown in Fig.1a and b. Some of peaks belonging to BaCO₃ could also be identified when calcined powders at 400°C. These minor impurity phases, however, gradually reduced with increase in calcinations temperature when powders were heated at 800°C. BaZrO₃ started to crystallize phase at 800°C as clear in Fig.1c. The crystallite size (d₁₁₀) is 19nm and the lattice constant (a) is 0.419nm according to (110) reflection in XRD result. The lattice constant is agreed very well with that reported in the literature as the standard value (JCPDS card #6.399).

Fig.2 shows that there is a two weight loses in the temperature ranges 100-400 and 400-750°C corresponding to losses of H₂O and CO₂ respectively. From the thermal analysis of the prepared precursor, we deduce that the temperature required for the formation of pure BaZrO₃ phase was 800°C as shown in Fig.2, therefore, calcinations of powders at 800°C is necessary.

Fig.3 shows the FTIR spectra obtained from precursor calcined at 250, 400, 600 and 800°C. The FTIR spectra of the calcined powders at 250°C (Fig.3a) shows a prominent band at 1425 cm⁻¹ and 1683 cm⁻¹ which assigned at bridged oxalate species[8]. Moreover very sharp bands can be observed at 1296, 912, and 806 cm⁻¹. The band at 1425 cm⁻¹ corresponds to asymmetric stretching of carbonate ions, while the band at 1060 cm⁻¹ corresponds to the symmetric stretching for CO₃²⁻ ion[9]. The main peak at 3400-3600 cm⁻¹ is due to the stretching mode of OH group.

Fig. 3b showed that the calcined powders at 400°C causes the increase of the band assigned at 1060 cm⁻¹ which associated to BaCO₃. Fig. 3b also shows a new band appearing at 1311 cm⁻¹ which assigned to ligated carbonate. Bands at 771, 619 and 486 cm⁻¹ observed in Fig. 3b have contributed from Zr-
O-Zr stretching mode[10]. Fig.3c shows that the 1419 cm\(^{-1}\) band as arising from the CO\(_2\) evolving species, since the TG curve (Fig.2) shows that some carbonate species must be existed up to 800\(^\circ\)C. Also, they existed in FTIR spectra of powders calcined at 600\(^\circ\)C as shown in Fig. 3c. Moreover, the crystalline BaZrO\(_3\) pure phase can be formed at 800\(^\circ\)C which displayed clearly in Fig. 3d.

The precursor (BaZrO(C\(_2\)O\(_4\))\(_2\).xH\(_2\)O) begins to lose its structural integrity at 250, 400, and 600\(^\circ\)C as measured by the disappearance of prominent IR bands at 478, 526cm\(^{-1}\) (Fig. 3a), 486, 619 and 771cm\(^{-1}\) (Fig.3b) and 1060cm\(^{-1}\) (Fig.3c).

**Conclusion**

Usage of oxalate method employing chloride precursors leading to the successful synthesis of phase pure barium zirconate (BaZrO\(_3\)) has been described. The precursor (BaZrO(C\(_2\)O\(_4\))\(_2\).xH\(_2\)O) begins to lose its structure and crystalline BaZrO\(_3\) has begin to form at 600\(^\circ\)C with some of impurities, while at 800\(^\circ\)C the precursors convert to crystalline BaZrO\(_3\) pure phase according to XRD results.
References

Fig. 1a: XRD patterns of the precursor (BaZrO(C₂O₄)₂·xH₂O.

Fig. 1b: XRD patterns of the calcined powder at 400°C.
Fig. 1c: XRD patterns of the calcined powder at 800°C.
Fig. 2: The weight loss of the precursor as a function of temperature.

Fig. 3a: FTIR spectra of the precursor calcined at 250°C.

Fig. 3b: FTIR spectra of the precursor calcined at 400°C.
Fig. 3c: FTIR spectra of the precursor calcined at 600°C.

Fig. 3d: FTIR spectra of the precursor calcined at 800°C.