

Phase and Morphology Evolution of Zirconium Titanate Powders

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ABSTRACT

In this work, the zirconium titanate, ZrTiO₄ was synthesized using a mixed oxide route. The formation of ZrTiO₄ as a function of calcinations temperature was determined from XRD results. The crystal structure, particle size distribution, morphology and phase composition of the calcined powders were investigated using XRD and SEM techniques. It was found that when the calcinations temperature reached 1150 °C the structure of the anatase-TiO₂ was changed to rutile-TiO₂. At 1350 °C calcinations, a single phase of ZrTiO₄ was formed and the yield was significantly increased, confirming the complete reaction between rutile-TiO₂ and ZrO₂. In conclusion, the pure wolframite phase of ZrTiO₄ powders could be obtained successfully using the simple mixed oxide route with calcinations condition of 1350 °C for 4 h at 5 °C /min.

Keywords: Zirconium titanate, ZrTiO₄, Calcination, Powder synthesis

INTRODUCTION

With the rapid progress of mobile and satellite communication systems such as cellular phones, global positioning systems (GPS), the dielectric ceramics at microwave frequency have been paid much attention for their applications in microwave resonators, wave guides, filters and micro-strip antennas in the past decade (Haertling, 1999; Moulson and Herbert, 1990). The three key requirements for a dielectric resonator are a high relative permittivity (ϵ_r) for possible miniaturization (because the size of a dielectric resonator $\propto 1/\epsilon_r^{1/2}$), a high unloaded quality factor (Q) for a stable resonant frequency, and a near-zero temperature coefficient of frequency (τ_f) for temperature stable circuits. Zirconium titanate (ZrTiO₄, ZT) based materials are widely used as dielectric resonators in telecommunications (Moulson and Herbert, 1990). Interest in these materials has grown because of their high resistivity and high dielectric constant which provides a high charge storage capacity. Moreover, the excellent temperature stability of microwave properties makes these materials particularly suitable for producing dielectric resonators in telecommunication systems (Cosentino, Muccillo and Muccillo, 2003). ZrTiO₄ has layered wolframite-type structure (ABO₄) of which the space group is $P2_1/a$. Figure 1 shows a unit cell of ZrTiO₄. Zr, Ti, and O atoms in ZrTiO₄ occupy Wyckoff positions 2f, 2e, and 4g, respectively (Harneit and Muller-

Buschbaum, 1993). $ZrTiO_4$ crystal consists of two kinds of octahedrons, ZrO_6 and TiO_6 , which form the layered structure by sharing the corners.

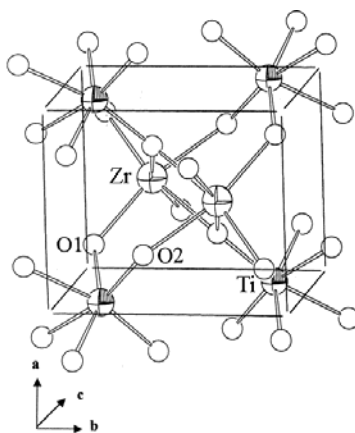
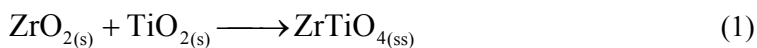


Figure 1 Schematic structure of $ZrTiO_4$ with the layered wolframite type modified from (Zou, Ye and Arakawa, 2001)

The purpose of this work was to perform a systematic study of the reaction between the starting ZrO_2 and TiO_2 precursors and to explore a simple conventional synthesis route for production of $ZrTiO_4$ powders. The phase formation characteristic of the powder, calcined at various calcinations temperature conditions, was also studied and discussed.

EXPERIMENTAL PROCEDURE

High purity oxide powders (>99%) of ZrO_2 and TiO_2 were used as starting materials. Powder-processing was carried out as shown schematically in figure 2. The starting materials were mixed, according to eqn (1):



and ball-milled in alcohol for 12 h following which the slurry was dried. After grinding and sieving with 100 mesh, seven calcination temperatures were selected to investigate the reaction to form zirconium titanate: 1000, 1050, 1100, 1150, 1250, 1300 and 1350 °C all for 4 h.

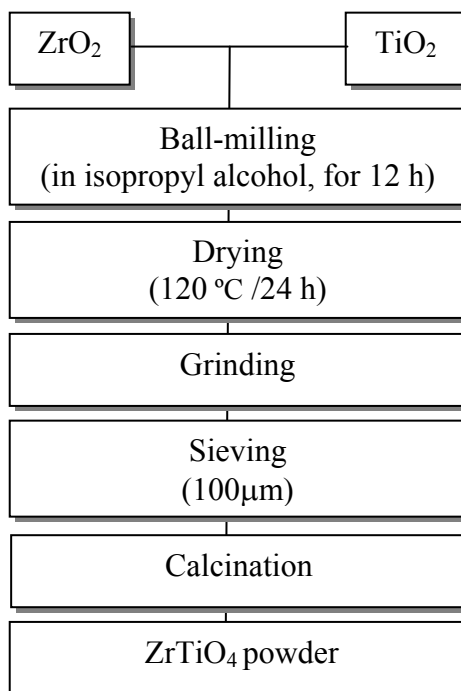


Figure 2 Preparation route for the ZrTiO_4 powder

The X-ray diffraction measurements were carried out on powdered samples using a high-resolution SIEMENS D 500 diffractometer. Filtered CuK_α $\lambda = 1.54056 \text{ \AA}$ (40 kV, 25 mA) was used. The diffraction diagram was measured from 20° to 60° in 2θ range with step size 0.02° (2θ) and 2 s counting time. The microstructure and grain growth of the calcined samples were examined using a scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Figure 3 shows XRD patterns of ZrTiO_4 powders at varying calcination temperatures. Sharp peaks of crystalline ZrO_2 and anatase- TiO_2 were detected at calcination temperature below $1,150^\circ\text{C}$. The phase analysis of ZrO_2 , rutile- TiO_2 , anatase- TiO_2 and ZrTiO_4 was carried out using Standard ICDD data. X-ray peak of precursors ZrO_2 , anatase- TiO_2 and rutile- TiO_2 can be matched with ICDD files numbers 37-1484, 21-1272 and 21-1276 respectively. The XRD patterns show that the transformation from anatase phase to rutile phase takes place as the calcination temperature increases, which was reported earlier by Monoharan et al. (Monoharan, Imhof, Thorne and Pine, 2000).

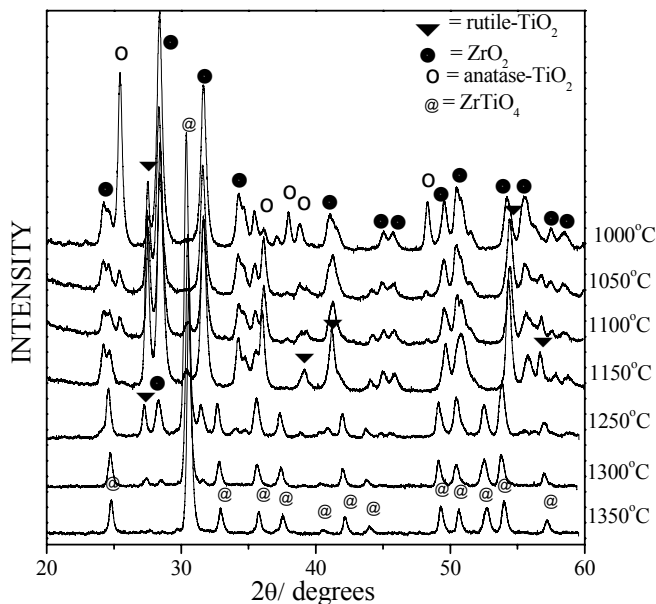


Figure 3 XRD patterns of ZrTiO_4 powder calcined at various temperatures for 4 h with heating/cooling rate of $5^\circ\text{C}/\text{min}$

The pure anatase phase, with its characteristic [101] reflection at $2\theta = 25^\circ$, persisted up to 1000°C . Rutile-related peaks began to appear at temperatures higher than 1050°C . The sample converted completely to rutile between 1100 and 1150°C , and no anatase-related peak was detected beyond these temperatures. It is well known that crystalline TiO_2 may exist in the following three polymorphisms: tetragonal rutile, tetragonal anatase or orthorhombic brookite. Among them rutile is the thermodynamically stable phase and the other two are metastable at high temperature.

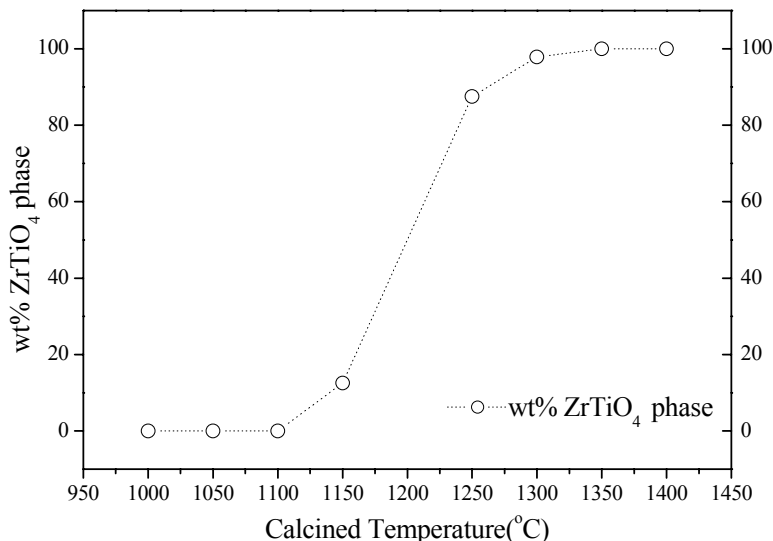


Figure 4 Percentage of wolframite phase as a function of calcinations temperature for ZrTiO₄ powders

Figure 4 shows the percentage of wolframite phase as a function of calcination temperature for ZrTiO₄ powders. The yield of ZrTiO₄ phase increased significantly until 1,350 °C, when a single phase of ZrTiO₄ was formed, revealing that rutile-TiO₂ had completely reacted with the ZrO₂ phase. No evidence of orthorhombic phase of Zr₅Ti₇O₂₄ was found. The relative proportions of ZrTiO₄, rutile-TiO₂, anatase-TiO₂ and monoclinic-ZrO₂ have been calculated according to the following approximate relationship, by analogy with our treatment of the yield of ZrTiO₄ in a related synthesis (Ananta, Brydson and Thomas, 1999):

$$wt\%ZrTiO_4\text{ phase} = \left(\frac{I_{ZrTiO_4}}{I_{ZrTiO_4} + I_{ZrO_2} + I_{TiO_2(r)} + I_{TiO_2(a)}} \right) \quad (2)$$

Here I_{ZrTiO_4} , I_{ZrO_2} , $I_{TiO_2(r)}$ and $I_{TiO_2(a)}$ refer to the intensities of the (111) wolframite peak, (111) baddeleyite-type structure peak, (110) rutile-TiO₂ peak and (101) anatase-TiO₂, respectively, these being the strongest reflections in all cases.

Because the raw materials used consist of multiphase, the formation reaction of the wolframite phase belongs to the heterogeneous system. A model used to treat multiphase reaction kinetics was derived by Johnson and Mehl and the equation for this reaction is

$$\ln[1/(1-y)] = (kt)^n \quad (3)$$

where y is the constant of the wolframite phase formed; k, the reaction rate constant; t, the calcination time; and n, the reaction order. The relation of $\ln \ln [1/(1-y)]$

versus $\ln t$ is plotted in figure 5. From this graph, it was found that the phase transformation of $ZrTiO_4$ obeys with the theory of transformations (Christian, 2002).

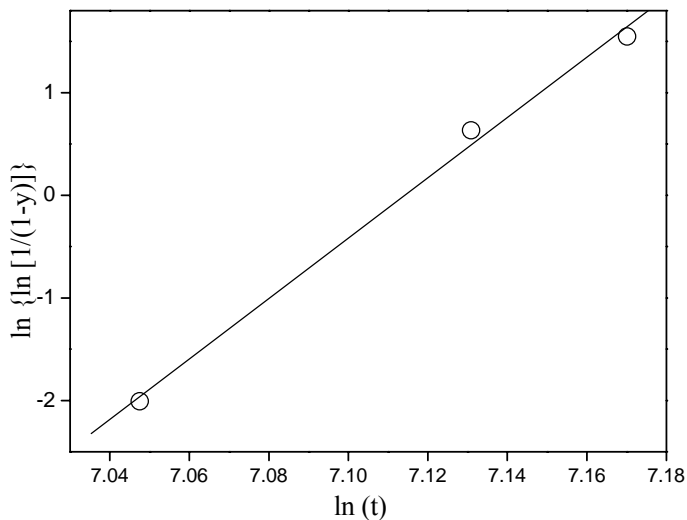


Figure 5 Reaction kinetics following the Johnson-Mehl-Avrami equation for $ZrTiO_4$

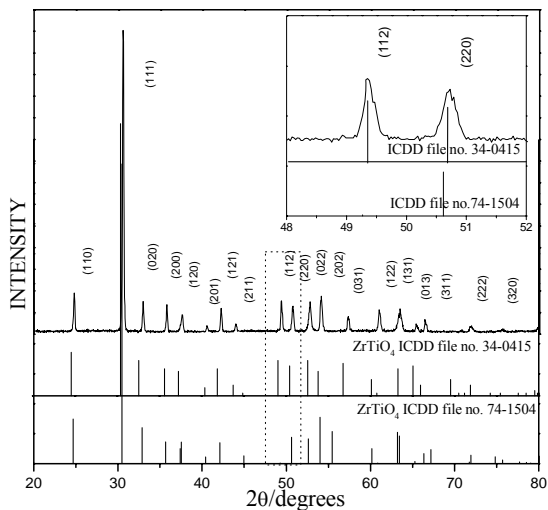


Figure 6 Computerised ICDD data-matching (file 34-0415) confirms the Formation of wolframite phase $ZrTiO_4$.

The strongest reflections apparent in the majority of the XRD patterns indicate the formation of zirconium titanate ($ZrTiO_4$) phases. These can be matched with ICDD file numbers 34-415 and 74-1504 (figure 6). The most obvious difference between the patterns for 34-415 and 74-1504 concerns the presence of an

additional (112) peak for the 34-415 pattern. In our experiment, the XRD patterns indicate the formation of an α - PbO_2 -type structure with orthorhombic symmetry zirconium titanate (ZrTiO_4) phases, which could be matched with ICDD file no. 34-415, with the lattice parameter, $a = 5.03 \text{ \AA}$, $b = 5.49 \text{ \AA}$, $c = 4.80 \text{ \AA}$. With the peaks properly indexed, lattice parameter was determined using UnitCell, a linear least squares refinement program. The orthorhombic unit cell was found to have the following dimensions: $a = 5.0184 (\pm 0.0006)$, $b = 5.4291 (\pm 0.0007)$ and $c = 4.7575 (\pm 0.005) \text{ \AA}$. These values are in good agreement with those reported by Zhang (Zhang, Li, Cao, Zhai and Zhang, 2001). The experimental work carried out here suggests that the optimal calcination conditions for single phase orthorhombic ZrTiO_4 is $1350 \text{ }^\circ\text{C}$ for 4 h with heating/cooling rates as fast as $5 \text{ }^\circ\text{C}/\text{min}$.

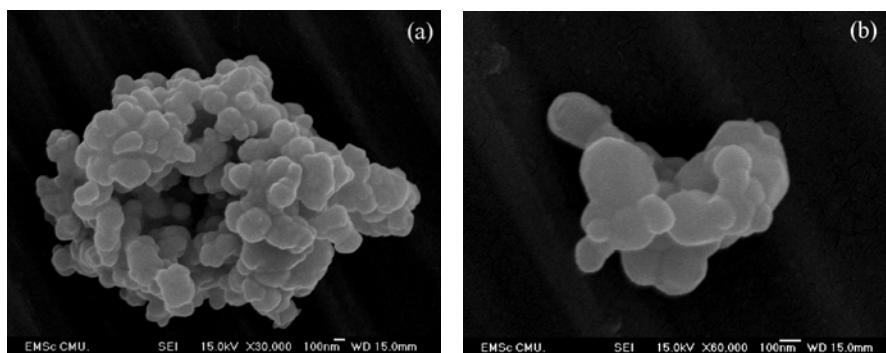


Figure 7 SEM micrographs of the ZrTiO_4 powders calcined at $1350 \text{ }^\circ\text{C}$ for 4 h with heating/cooling rate $5 \text{ }^\circ\text{C}/\text{min}$

SEM micrographs of the calcined ZrTiO_4 powders are given in figure 7(a) and 7(b). In General, the particles are agglomerated and basically irregular in shape, with a substantial variation in particle size and morphology. Particle size can be estimated from SEM micrographs to be in the range of 70-300 nm. A detailed study at high magnification (figure 7(b)) showed that they had spherical secondary particles, composing of nano-sized primary particulates.

CONCLUSIONS

Polycrystalline pellets of ZrTiO_4 were synthesized using solid state synthesis using oxides as starting materials. It was found that when the calcinations temperature reached $1150 \text{ }^\circ\text{C}$ the structure of the anatase- TiO_2 was changed to rutile- TiO_2 . At $1350 \text{ }^\circ\text{C}$ calcinations, a single phase of ZrTiO_4 was formed and the yield was significantly increased, confirming the complete reaction between rutile- TiO_2 and ZrO_2 . Evidence has been obtained for a 100% yield of ZrTiO_4 at a calcination temperature of $1350 \text{ }^\circ\text{C}$ for 4 h with heating/cooling rates of $5 \text{ }^\circ\text{C}/\text{min}$. XRD showed the compound to be the wolframite structure, having orthorhombic lattice parameters of $a = 5.0184 (\pm 0.0006)$, $b = 5.4291 (\pm 0.0007)$ and $c = 4.7575 (\pm 0.005) \text{ \AA}$. Particle size can be estimated from SEM micrographs to be in the range of 70-300 nm.

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