

Synthesis and a crystal structural study of microwave dielectric Zirconium Titanate ($ZrTiO_4$) powders via a mixed oxide synthesis route

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A mixed oxide synthesis route has been investigated for the synthesis of zirconium titanate, $ZrTiO_4$. The formation of $ZrTiO_4$ phases have been investigated as a function of calcination temperature by XRD. The crystal structure, particle size distribution, morphology and phase composition of the calcined powders were determined via XRD and SEM. It has been found that with increasing calcination temperature up to 1150°C , the results showed that anatase- TiO_2 changed structure to rutile- TiO_2 . The yield of the $ZrTiO_4$ phase increased significantly up to 1350°C , when a single phase of $ZrTiO_4$ was formed, revealing that the rutile- TiO_2 had completely reacted with the ZrO_2 phase. It seemed that the pure wolframite phase of $ZrTiO_4$ powders was successfully obtained from calcinations conditions of 1350°C for 4 h with heating/cooling rates of 5 Kminute^{-1} .

Key words: Zirconium titanate, $ZrTiO_4$, Calcination, Powder synthesis.

Introduction

With the rapid progress of mobile and satellite communication systems such as cellular phones, global positioning systems (GPS), dielectric ceramics at microwave frequencies have received much attention for their applications in microwave resonators, wave guides, filters and micro-strip antennas in the past decade [1, 2]. 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 [1]. Zirconium titanate ($ZrTiO_4$, ZT) based materials are widely used as dielectric resonators in telecommunications [1]. 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 their microwave properties makes these materials particularly suitable for producing dielectric resonators in telecommunication systems [3].

$ZrTiO_4$ has a layered wolframite-type structure (ABO_4) of which the space group is $P2_1/a$. Figure 1 shows a unit cell of $ZrTiO_4$. Zr, Ti, and O atoms in $ZrTiO_4$ occupy Wyckoff positions 2f, 2e, and 4g, respectively [4]. A $ZrTiO_4$ crystal consists of two kinds of octahedra, ZrO_6 and TiO_6 , which form the layered structure by sharing the corners. The purpose of this study was to perform a systematic investigating of the reaction between the

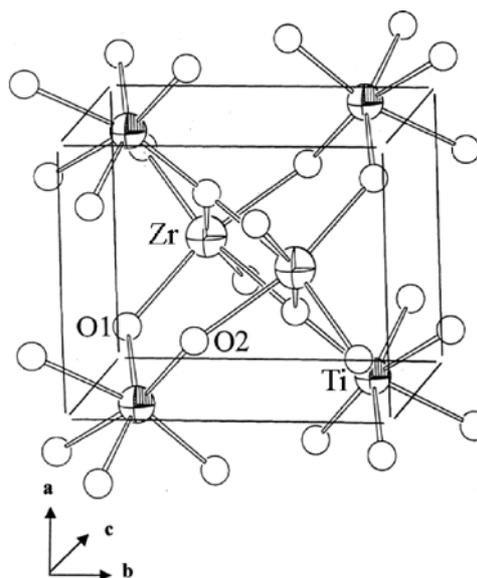


Fig. 1. Schematic structure of $ZrTiO_4$ with a layered wolframite type structure (modified from Zou et al. [9]).

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 calcination temperatures, was also studied and will be 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 Fig. 2. The starting materials were mixed, according to eqn (1):

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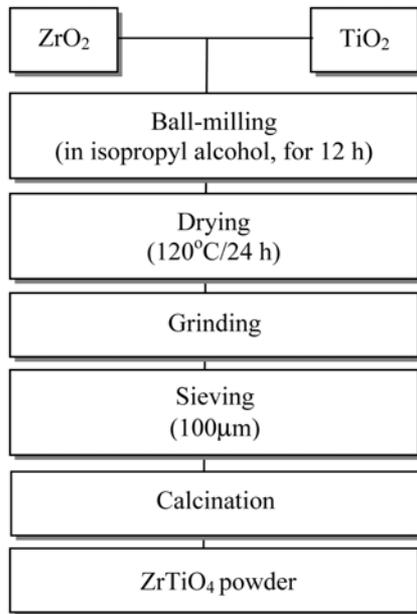


Fig. 2. Preparation route for the $ZrTiO_4$ powder.



and ball-milled in alcohol for 12 h after which the slurry was dried. After grinding and sieving with 100 μm mesh, seven calcination temperatures were selected to investigate the reaction to form zirconium titanate: 1000, 1050, 1100, 1150, 1250, 1300 and 1350 $^{\circ}\text{C}$ all for 4 h. The X-ray diffraction measurements were carried out on powdered samples using a high-resolution SIEMENS D 500 diffractometer. Filtered $\text{CuK}\alpha$ $\lambda = 1.54056 \text{ \AA}$ (40 kV, 25 mA) was used. The diffraction patterns were measured from 20° to 60° in 2θ range with a step size of 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 1150 $^{\circ}\text{C}$. 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 the anatase phase to the rutile phase takes place as the calcination temperature increases, which was reported earlier by Monoharan et al. [5].

The pure anatase phase, with its characteristic [101] reflection at 28 to 25° , persisted up to 1000 $^{\circ}\text{C}$. Rutile-related peaks began to appear at temperatures higher than 1050 $^{\circ}\text{C}$. The sample converted completely to rutile

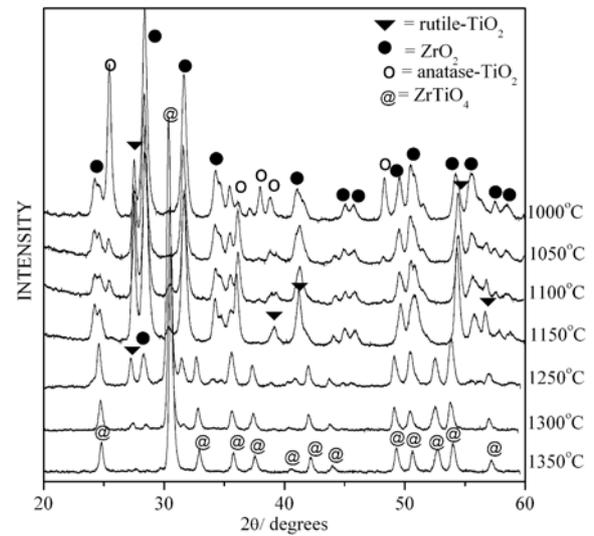


Fig. 3. XRD patterns of $ZrTiO_4$ powder calcined at various temperatures for 4 h with a heating/cooling rate of 5 Kmin^{-1} .

between 1100 and 1150 $^{\circ}\text{C}$, 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 these rutile is the thermodynamically-stable phase and the other two are metastable at high temperature.

Figure 4 shows the percentage of wolframite phase as a function of calcination temperature for $ZrTiO_4$ powders. The yield of $ZrTiO_4$ phase increased significantly up to 1350 $^{\circ}\text{C}$, when a single phase of $ZrTiO_4$ was formed, revealing that the rutile- TiO_2 had completely reacted with the ZrO_2 phase. No evidence of an orthorhombic phase of $Zr_5Ti_7O_{24}$ was found.

The relative proportions of $ZrTiO_4$, rutile- TiO_2 , anatase- TiO_2 and monoclinic- ZrO_2 have been calculated according to the following approximate relationship, by analogy with our treatment of the yield of $ZrTiO_4$ in a related synthesis [6]:

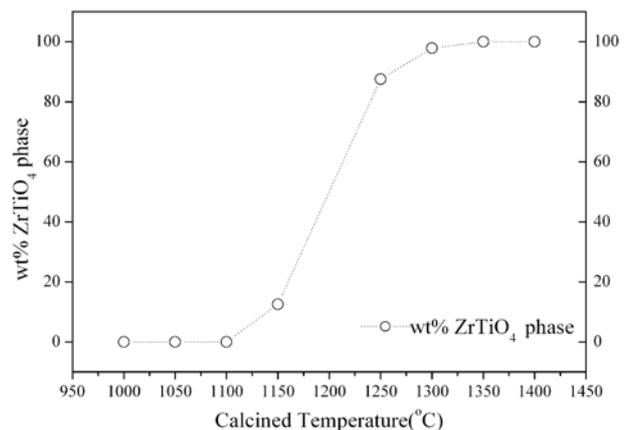


Fig. 4. Percentage of wolframite phase as a function of calcination temperature for $ZrTiO_4$ powders.

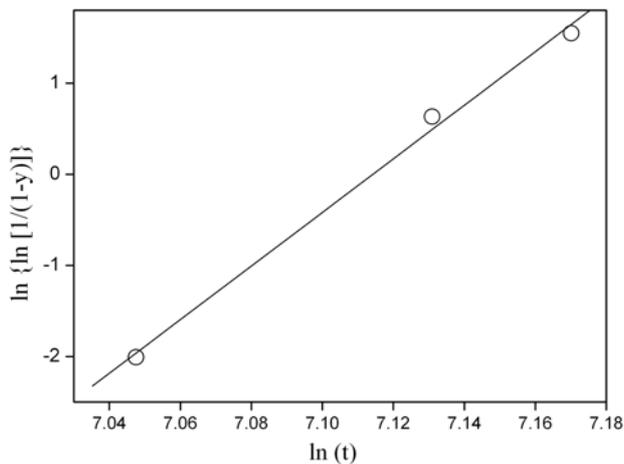


Fig. 5. Reaction kinetics following the Johnson-Mehl-Avrami equation for ZrTiO_4 .

$$\text{wt\% ZrTiO}_4 \text{ phase} = \left(\frac{I_{\text{ZrTiO}_4}}{I_{\text{ZrTiO}_4} + I_{\text{ZrO}_2} + I_{\text{TiO}_2(\text{r})} + I_{\text{TiO}_2(\text{a})}} \right) \quad (2)$$

Here I_{ZrTiO_4} , I_{ZrO_2} , $I_{\text{TiO}_2(\text{r})}$ and $I_{\text{TiO}_2(\text{a})}$ refer to the intensities of the (111) wolframite peak, (111) baddeleyite-type structure peak, (110) rutile- TiO_2 peak and (101) anatase- TiO_2 , respectively, these being the strongest reflections in all cases.

Because the raw materials used consist were multiphase, the formation reaction of the wolframite phase belongs to an 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 Fig. 5. From this graph, it was found that the phase transformation of ZrTiO_4 obeys this theory of the transformations [7].

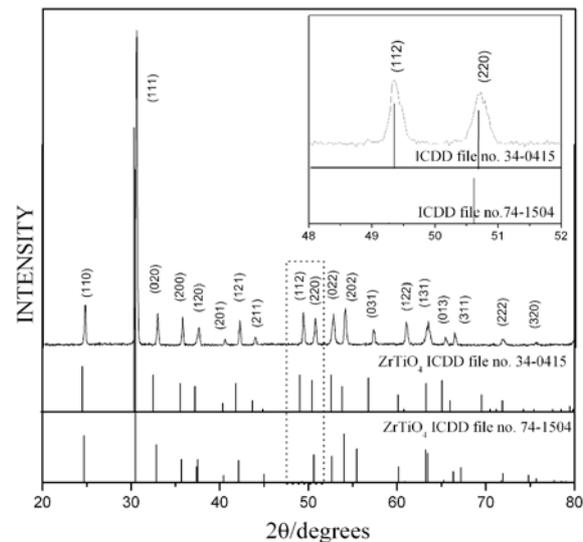


Fig. 6. Computerised ICDD data-matching (file 34-0415) confirms the formation of the wolframite phase ZrTiO_4 .

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 (Fig. 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 lattice parameters, $a = 5.03 \text{ \AA}$, $b = 5.49 \text{ \AA}$, $c = 4.80 \text{ \AA}$. With the peaks properly indexed, lattice parameters were determined using Unit-Cell, 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 et al. [8]. The

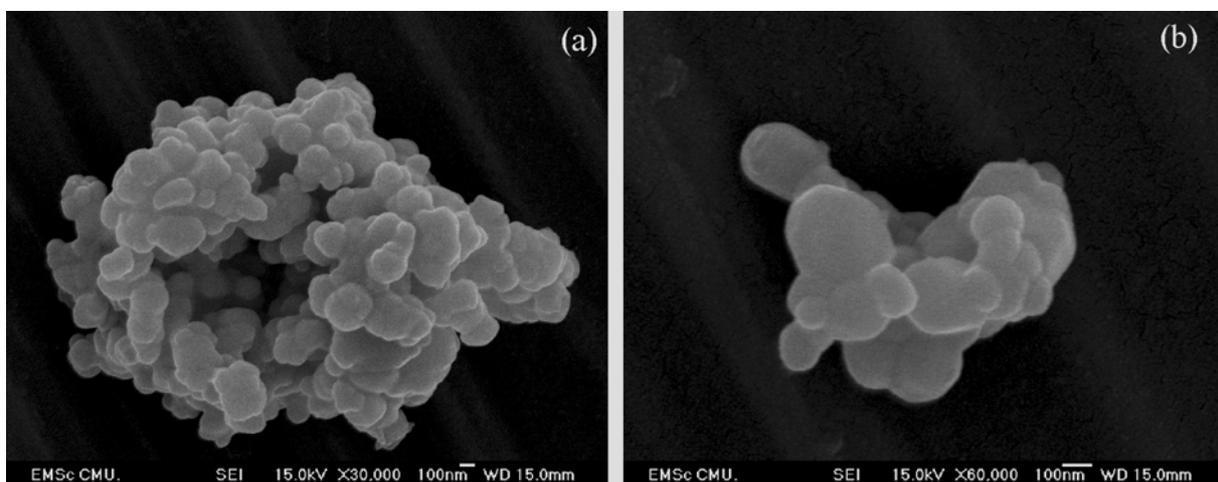


Fig. 7. SEM micrographs of the ZrTiO_4 powders calcined at $1350 \text{ }^\circ\text{C}$ for 4 h, with heating/cooling rate 5 Kminute^{-1} .

experimental work carried out here suggests that the optimal calcination conditions for single phase orthorhombic $ZrTiO_4$ is 1350 °C for 4 h with heating/cooling rates as fast as 5 Kminute⁻¹.

SEM micrographs of the calcined $ZrTiO_4$ powders are given in Fig. 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. The particle size can be estimated from SEM micrographs to be in the range of 70-300 nm. A detailed study at higher magnification (Fig. 7(b)) showed that the particles had spherical secondary particles, composed of nano-sized primary particulates.

Conclusions

Polycrystalline pellets of $ZrTiO_4$ were synthesized using solid state synthesis using oxides as starting materials. Evidence has been obtained for a 100% yield of $ZrTiO_4$ at a calcination temperature of 1350 °C for 4 h with heating/cooling rates of 5 Kminute⁻¹. XRD showed the compound to have the wolframite structure, having orthorhombic lattice parameters of $a = 5.0184$ (± 0.0006), $b = 5.4291$ (± 0.0007) and $c = 4.7575$ (± 0.005) Å.

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