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Preparation, microstructure and microwave dielectric properties of $Zr_xTi_{1-x}O_4$ ($x = 0.40$–0.60) ceramics

S.X. Zhang *, J.B. Li, J. Cao, H.Z. Zhai, B. Zhang

State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering,
Tsinghua University, Beijing 100084, China

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Abstract

$Zr_xTi_{1-x}O_4$ ($x = 0.40$–0.60) ceramics sintered without additives were prepared from powders made by the coprecipitation of metal salts from aqueous solutions in order to investigate the existence range of a homogeneous phase and the relationships between composition, microstructure and the dielectric properties. XRD, TEM, SEM, EDS, and the dielectric measurements were used to characterize the products. A homogeneous solid solution was obtained. Its crystal structure was isomorphous with $ZrTiO_4$. The variation of the lattice parameters with TiO_2 content was discussed. The optimum sintering temperature of samples was dependent of composition. TiO_2 suppressed the densification and acted as a grain growth enhancer during the sintering process. With the increase in TiO_2 content the relative densities of the sintered bodies decrease, while the grain sizes increase. The dielectric properties at microwave frequency (1.8 GHz) in this system, especially Q value, were poor, due to low densification, impurities and lattice defects. The dielectric constant ε_r and Q value exhibited a significant dependence on the relative density and composition. Both ε_r and Q increased with the increase in relative density, but they were primarily influenced by the composition and the effect of the relative density could be ignored when the relative density was greater than 90% theoretical. ε_r increased slightly with increasing TiO_2 content, while Q value decreased.

Keywords: Dielectric properties; Microwave dielectrics; Sintering; $(Zr,Ti)_2O_4$

1. Introduction

Communication at microwave frequencies has been required with advances in communication networks. Many kinds of dielectric materials have been investigated for microwave applications.[1–4] Among them, zirconium titanate ($ZrTiO_4$)-based ceramics, which have a high dielectric constant, a high Q value and a low temperature coefficient of resonant frequency, are received special attention.[5–7] Many papers focused on improving the microwave dielectric properties of $ZrTiO_4$-based ceramics with various kinds of additives.[8–13]

$ZrTiO_4$ can be prepared by solid state reaction between ZrO_2 and TiO_2 at elevated temperature (1200–1600°C) and long heating times.[14] For these reasons various chemical methods have been developed in order to produce reactive precursors to yield $ZrTiO_4$ powders by thermal treatment at lower temperature.[15–18] $ZrTiO_4$-based ceramics are often processed with sintering additives. It is difficult to fully density $ZrTiO_4$ without sintering additives. Sintering aids used for $ZrTiO_4$-based ceramics are added as a combination of two or more oxides from ZnO, CuO, NiO, La_2O_3 etc.[7–13] These additives, however, lead to the degradation of its dielectric properties, due to the formation of second phase at grain boundaries. Therefore, reduction of the amounts of additives has been required for improvement of the dielectric properties. The chemical preparation of reactive precursors, especially by the coprecipitation route which utilizes solution chemistry, offers advantages over traditional processing techniques because of the fined grained powders, better homogeneity obtained and the lower processing temperature. The densification and the dielectric properties of $ZrTiO_4$-based ceramics may be improved if the samples are prepared from powders made by the coprecipitation method and sintered without additives. But, until now it seems not to be concerned in the other literatures.

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* Corresponding author.

E-mail address: zhang-shx@263.net (S.X. Zhang).

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In this paper results are presented for the production and the microwave dielectric properties of $ZrTiO_4$ solid solutions, $Zr_xTi_{1-x}O_4$ ($x = 0.40$–0.60) ceramics, which are prepared from powders made by the coprecipitation of metal salts from aqueous solutions and sintered without additives. Our study is concerned with the dielectric properties of samples made by the chemical method and the relation of some physical properties of $ZrTiO_4$ solid solutions, $Zr_xTi_{1-x}O_4$ ($x = 0.40$–0.60) to the composition. Five compositions are selected to span the $ZrTiO_4$ solid solution range based on the ZrO_2–TiO_2 phase diagram.[19]

2. Experimental procedure

2.1. Materials and preparation

$Zr_xTi_{1-x}O_4$ ($x = 0.40$, 0.45, 0.50, 0.55, 0.60) powders were synthesized as follows. A 0.5 mol/l aqueous solution of zirconium oxychloride and titanium sulfate in the requisite Zr/Ti molar ratio of the desired product was dropped into extensive dilute ammonia solution with pH maintained at 9 ± 0.1 under stirring to produce coprecipitate of Zr–Ti hydroxides. The precipitates were filtered, washed with deionized water to remove the anions taken into the precipitates by the starting materials. Next, the precipitates were washed with absolute alcohol for dewatering. Finally, the precipitates were dried in an oven overnight at 80°C. The powders obtained were termed as starting powders A through E. The starting powders were calcined at 800°C for 1.5 h. The calcined powders, after they were remilled with an organic dispersant and binder, were molded into disks 10 mm in diameter and 2–5 mm thick under a pressure of 100 MPa and then were sintered in air at various temperatures (1400, 1450, 1500, 1550, 1600°C) for 4 h and cooled with the furnace.

2.2. Characterization of powders and products

Thermal analysis (TG,DTA)(TGA 92, Setaram, France) was conducted on the starting powders at a heating rate of 10°C/min under flowing air. X-ray diffraction (XRD) analysis (D/Max-IIIB, Rigaku, Japan) was used to identify the crystalline phases of the calcined powders and the sintered samples. Lattice parameters of $ZrTiO_4$($ZrTiO_4$ solid solutions) were determined by referring to an external standard of silica. A transmission electron microscope (TEM)(JEM-200CX, Jeol, Japan) was applied to observe the morphology of the calcined powders.

The bulk densities of the sintered bodies were measured by the Archimedes method. The as-sintered surfaces of the samples were observed by scanning microscopy (SEM)(JSM-6301F, Jeol, Japan) and energy dispersive X-ray spectrometry (EDS)(Link ISIS-300, UK). The average grain size was determined by measuring the mean linear intercept of the grains as described by Mendelson.[20] Dielectric properties at microwave frequencies were measured by the dielectric rod resonator method using cylindrical specimens.[21] The measurement instruments were an HP 4291B impedance analyzer. Silver paste was used for the electrodes.

3. Results and discussion

3.1. Formation and crystal structure

All starting powders are amorphous. Thermogravimetric examination shows weight losses of ~20% at 170°C in all starting powders. These can be attributed to the release of absorbed and hydrated water. Differential thermal analysis curves for all starting powders show sharp exothermic peaks. The peaks are found to result from the crystallization of $ZrTiO_4$ phase. The data in Table 1 show that the temperature of crystallization is shifted to higher temperatures from A to C, but then to lower temperatures from C to E. In addition, the height of the peaks changes with composition; with increasing TiO_2 content, it increases between 40 and 50 mol% TiO_2 and decreases between 50 and 60 mol% TiO_2.

X-ray diffraction patterns show the calcined powders are a single phase $ZrTiO_4$, which indicate the formation of the $ZrTiO_4$ solid solution between 40 and 60 mol% TiO_2. Fig. 1 shows XRD patterns of the calcined powders with the various compositions prepared. The patterns are in agreement with those for $ZrTiO_4$ and take place with slight peak shifts to greater 2-theta value with TiO_2 content increasing in the product. Using Scherer's equation, the average particle-size of the calcined powder is calculated from the line broadening of XRD peaks. TEM observations further confirm that the particles have a mean particle-size of 20–30 nm appearing with a spherical morphology and having a simple mode of size-distribution. Fig. 2 shows a representative TEM image of $Zr_xTi_{1-x}O_4$ ($x = 0.40$–0.60) particles. It reveals that the powders have a lower agglomeration.

Table 1
Chemical compositions and crystallization temperature of starting powders

Starting powder	Composition (mol%)		Crystallization temperature (°C)
	ZrO_2	TiO_2	
A	40	60	680–690
B	45	55	695–710
C	50	50	700–715
D	55	45	690–710
E	60	40	685–705

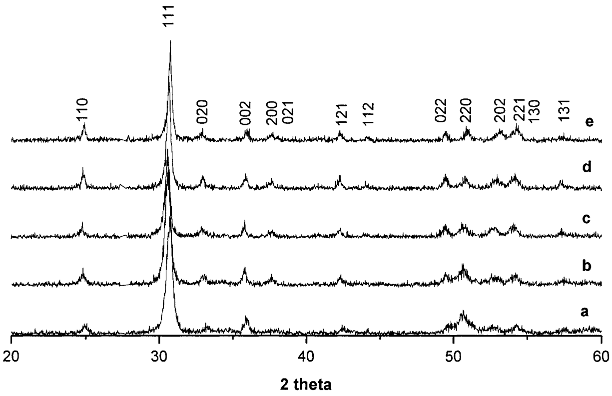

Fig. 1. XRD patterns of $Zr_xTi_{1-x}O_4$ calcined powders. x: a. 0.40; b. 0.45; c. 0.50; d. 0.55; e. 0.60.

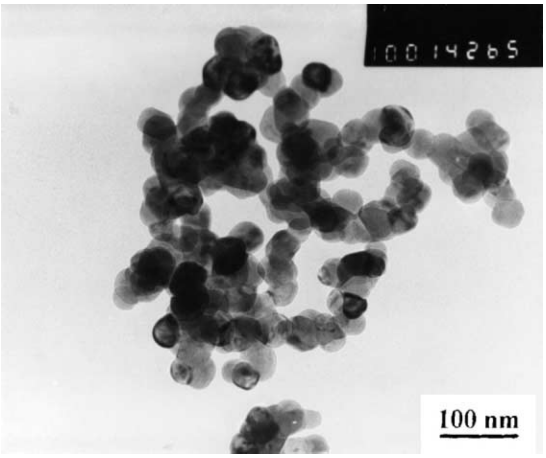

Fig. 2. TEM of the $Zr_xTi_{1-x}O_4$ ($x=0.50$) calcined powders.

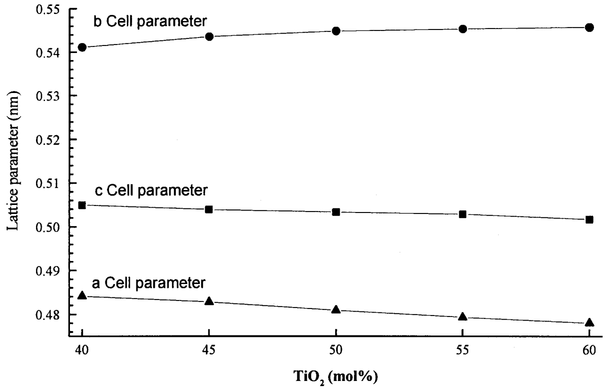

Fig. 3. Lattice parameters for $ZrTiO_4$ phase as a function of composition.

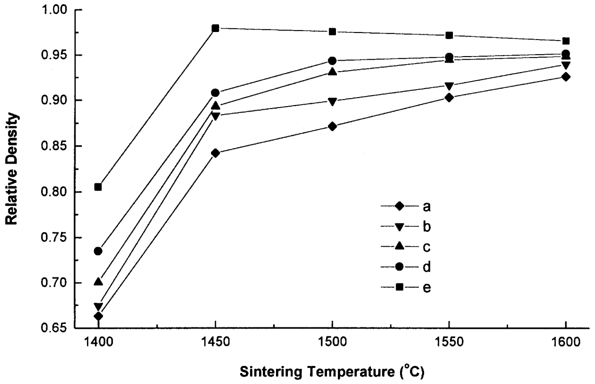

Fig. 4. Relative density of $Zr_xTi_{1-x}O_4$ ceramics as a function of sintering temperature. x: a. 0.40; b. 0.45; c. 0.50; d. 0.55; e. 0.60.

Crystallographic analyses indicate that the structure of $Zr_xTi_{1-x}O_4$ ($x=0.40$–0.60) is orthorhombic with a space group Pbcn. The lattice parameters are determined by obtained XRD patterns. The corresponding values of lattice parameters for $Zr_xTi_{1-x}O_4$ ($x=0.40$–0.60) are shown in Fig. 3; with increasing TiO_2 content, the lattice parameters a and c decrease from 0.4841 to 0.4780 nm and from 0.5049 to 0.5017 nm, respectively, whereas the lattice parameter b increases from 0.5411 to 0.5457 nm. The value of the unit cell decreases continuously from 0.1323 to 0.1309 nm^3 with increasing TiO_2 content. Compared to the product prepared by the solid-state reaction, the lattice parameters have more significant variations with the compositional change.[19]

3.2. Densification and microstructure

The relative densities of green bodies are around 60% of the theoretical value. Sintered products of all compositions are light yellow in color. With the increase of TiO_2 content, the color becomes darker and tends to a light brown. The relative densities of sintered bodies range from 66 to 98% of the theoretical value depending on the sintering temperature and composition. No significant improvement of densification is obtained compared to that prepared by the mixed oxide method with sintering additives.[7,22] Fig. 4 shows the relative densities of sintered bodies as a function of sintering temperature. The relative densities of all samples quickly increase as the sintering temperature increases from 1400 to 1450°C. With continued increases in sintering temperature the relative densities of the samples with $x=0.40$–0.55 slowly increase, while that of the sample with $x=0.60$ slightly decrease. With the same sintering temperature, the relative densities decrease with increases in TiO_2 content. These results indicate the optimum sintering temperature of $Zr_xTi_{1-x}O_4$ ($x=0.40$–0.60) ceramics is dependent of composition and TiO_2 affects the densification. For systems which do not densify significantly, vapour transport and surface diffusion have been suggested as the predominant mass transport mechanisms. Vapour transport occurs by an evaporation-condensation process and the extent to which it occurs depends on the vapour pressure of the material being sintered. For most oxides in use as ceramics, vapour phase transport is usually only of importance at very high temperatures, close to the melting point. In the ZrO_2–TiO_2 system, owing to the low volatility of zirconium and titanium oxide,[23] it is to be expected that surface diffusion would play a major role in the coarsening process at low temperature. TiO_2 might act to inhibit sintering in $Zr_xTi_{1-x}O_4$ ($x=0.40$–0.60) ceramics by increasing the surface diffusion coefficient in the material and hence increasing the coarsening rate. Other researchers agree that TiO_2 additions accelerate grain growth and act to suppress densification in Y_2O_3–TZP ceramics.[24,25]

The typical microstructures of the as-sintered surfaces of $Zr_xTi_{1-x}O_4$ ($x=0.40$–0.60) ceramics are shown in Fig. 5. SEM micrographs show grains are rounded and uniform in shape and few pores at grain boundaries or triple points; cracks or microcracks are not observed. The change in average grain size with composition is clearly noticeable. In the ceramic with $x=0.60$, grain growth is discontinuous-type. The grains may be divided into two different size ranges. The fraction of large grains is higher than small grains. As x decreases in these ceramics, the discontinuous-type of grain growth is suppressed. However, the average grain size increases. The micrograph of a sample with $x=0.50$ shows uniform grains, with an average grain size of 12.7 μm. A further decrease in x enhances the grain growth as shown in the micrograph of a sample with $x=0.40$. As expected from the previous discussions, in solid solution, TiO_2 suppresses the densification, this leading to grain growth when attempts are made to attain higher densities. TiO_2 acts as a grain growth enhancer during the sintering process.

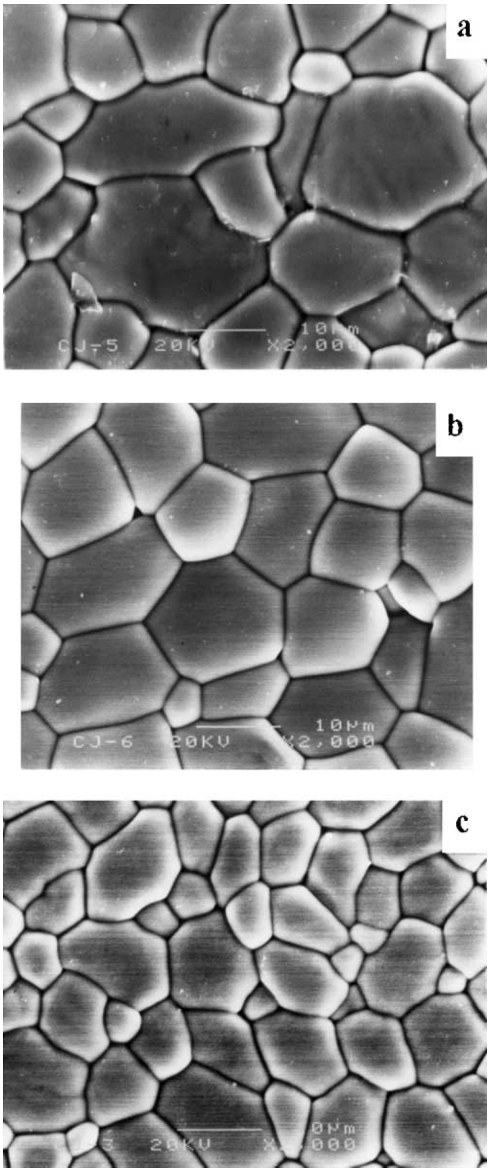

Fig. 5. SEM micrographs of $Zr_xTi_{1-x}O_4$ ceramics sintered at 1600°C/4 h. a. $x=0.40$; b. $x=0.50$; c. $x=0.60$.

A secondary phase is not observed in the XRD patterns of the sintered bodies and the patterns are in agreement with those for $ZrTiO_4$. EDS analyses show that sample compositions are homogeneous with no distinction between the grains and the grain boundaries, and no evidence of segregation of the main components (Ti or Zr).

3.3. Microwave dielectric properties

The microwave dielectric properties were measured at 1.8 GHz. $Zr_xTi_{1-x}O_4$ ($x=0.40$–0.60) ceramics, which were prepared from the powders made by the coprecipitation route and sintered without additives, show poor dielectric properties, especially lower Q value

The dielectric properties are thought to be affected by a combination of second phases, microstructural defects, specimen density, impurities and lattice defects.[7] In our study, no additives were used and no microstructural defects e.g. voids and microcracks were observed by SEM. So the poor dielectric properties of samples primarily result from specimen density, impurities and lattice defects.

The residual porosity monitored by the sintered density, will affect both dielectric constant ε_r and quality factor Q. The effect of porosity on dielectric constant can be estimated via the law of mixtures approach e.g. the Lichtenecker equation[26]

$$\log\varepsilon_r = \Sigma \log\varepsilon_i V_i$$

where ε_r is the dielectric constant of the product, ε_i is the dielectric constant of the ith phase, V_i is the volume fraction of the ith phase and porosity is regarded as a phase with a dielectric constant of 1. Increasing the amount of porosity will reduce the overall dielectric constant. Pores may also cause a reduction in Q value, but the effect cannot be easily quantified. The relationship between density and Q value is not readily explained. It is assumed that for materials of density less than 90% theoretical, the decrease in Q value, due to increasing porosity may be attributed to the effects of polarization at the pore surface.[8]

The dielectric constants ε_r and the quality factors Q of $Zr_xTi_{1-x}O_4$ ($x = 0.40$–0.60) ceramics are shown as a function of sintering temperature in Figs. 6 and 7, respectively. Without additives, the ε_r values range from 19 to 43 and the Q values range from 240 to 840 depending on the sintering temperature and composition. A comparison of Fig. 4 with Figs. 6 and 7 shows that ε_r and Q increase as the relative density increases, but they are primarily influenced by the composition and the effect of the relative density can be ignored when the relative density is greater than 90% theoretical.[8] Fig. 8 shows ε_r and Q of the samples sintered at 1600°C/4 h as a function of the composition. With this temperature, densities of all samples are great than 90%. The results show that ε_r increases slightly with increasing TiO_2 content, while Q decreases, because TiO_2 have a higher ε_r and a lower Q value.[27]

The ε_r values for our samples are in excellent agreement with data reported for $ZrTiO_4$ ceramics prepared via different routes,[7,15,18,22] but the Q values are unusually low compared to that reported by other author.[7,15,18] The lower Q values, not only result from poor densification, but also result from the following reasons. On the one hand, in many complex perovskites, cation ordering has been shown to lead to a significant improvement of dielectric properties. The increase in Q value by up to a factor of 10 for the complex perovskites, concurrent with increase in cation ordering, is believed to be caused by the reduction in lattice strain associated with the segregation of cations.[3,7] In our processing, the samples cooled with the furnace may be regarded as the approximation to the high temperature disordered form of $ZrTiO_4$. The disordered form of $ZrTiO_4$ possesses a low Q value. On the other hand, $Zr_xTi_{1-x}O_4$ ($x = 0.40$–0.60) ceramics prepared from powders made by the coprecipitation of $ZrOCl_2$ and $Ti(SO_4)_2$. $Ti(SO_4)_2$ contained small amounts of Fe (0.01 wt.%). In addition, we prepared pellets by stainless-steel die. So the samples also contain Fe impurities. It is suggested that Fe impurities cause a degradation of Q value and the Fe ions diffuse into the lattice, possibly replacing Zr and/or Ti producing oxygen vacancies lattice defects.[4] The presence of the impurity ions in the host lattice modify the lattice vibration modes (which ultimately define ε_r and Q), and effectively reduce the Q value.

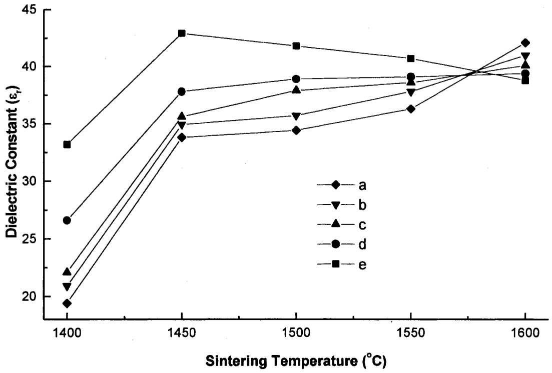

Fig. 6. Dielectric constant (ε_r) of $Zr_xTi_{1-x}O_4$ ceramics as a function of sintering temperature. x: a. 0.40; b. 0.45; c. 0.50; d. 0.55; e. 0.60.

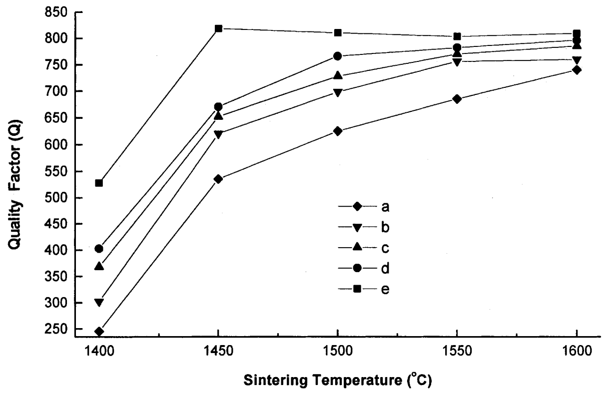

Fig. 7. Quality factor (Q) of $Zr_xTi_{1-x}O_4$ ceramics as a function of sintering temperature x: a. 0.40; b. 0.45; c. 0.50; d. 0.55; e. 0.60.

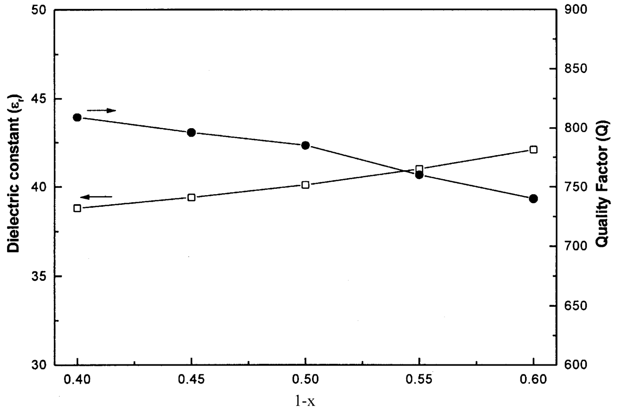

Fig. 8. Microwave dielectric properties of $Zr_xTi_{1-x}O_4$ ceramics as a function of $1-x$.

For the above reasons our $Zr_xTi_{1-x}O_4$ ($x = 0.40$–0.60) ceramics show poor dielectric properties, especially unusually low Q value. In principle, the higher dielectric properties of $Zr_xTi_{1-x}O_4$ ($x = 0.40$–0.60) ceramics should be achieved in high sintered density, free of impurities and lattice defects.

4. Conclusions

1. $ZrTiO_4$ solid solutions, $Zr_xTi_{1-x}O_4$ ($x = 0.40$–0.60) prepared by the coprecipitation of zirconium and titanium metal salts crystallize at low temperature from amorphous materials between 40 and 60 mol% TiO_2. As zirconium is substituted for titanium, the solid solutions can be indexed in an orthorhombic unit cell with a and c decreasing from 0.4841 to 0.4780 nm and from 0.5049 to

0.5017 nm, respectively, and *b* increasing from 0.5411 to 0.5457 nm. The volume of the unit cell decreases continuously with increasing TiO_2 content.

2. The optimum sintering temperature of $Zr_xTi_{1-x}O_4$ ($x=0.40$–0.60) ceramics is dependent of composition. TiO_2 suppresses the densification and acts as a grain growth enhancer during the sintering process. With the increase in TiO_2 content the relative densities of the sintered bodies decrease, while the grain sizes increase.
3. $Zr_xTi_{1-x}O_4$ ($x=0.40$–0.60) ceramics, which were prepared from the powders made by the coprecipitation route and sintered without additives, show poor dielectric properties, especially lower *Q* value, due to low densification, impurities and lattice defects. The dielectric constant ε_r and the quality factor *Q* are greatly affected by the relative density and composition. Both ε_r and Q increase as the relative density increases, but they are primarily influenced by the composition and the effect of the relative density can be ignored when the relative density is greater than 90% theoretical. ε_r increase slightly with increasing TiO_2 content, while *Q* value decrease.

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