

# Hydrothermal synthesis and characterization of crystalline $Zr_xTi_{1-x}O_4$ ( $x = 0.35\text{--}0.65$ ) powders as a precursor for the preparation of $PbZr_xTi_{1-x}O_3$

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A series of crystalline  $Zr_xTi_{1-x}O_4$  ( $x = 0.35\text{--}0.65$ , ZT) powders have been hydrothermally synthesized from double hydrous oxides under moderate conditions. The influences of some factors such as the precursor, pH of medium and anions on the formation of the product have been investigated. The solid-state reaction of ZT powder with PbO has been studied. XRD, TEM and other techniques have been used to characterize the product in detail. The ZT powder has a mean particle-size of 10–30 nm and as a precursor appears to have high reactivity to form  $PbZr_xTi_{1-x}O_3$  (PZT). © 1999 Kluwer Academic Publishers

## 1. Introduction

Zirconium titanate ( $Zr_xTi_{1-x}O_4$ , ZT,  $x = 0.35\text{--}0.65$ ) has been shown to be an effective acid-base bifunctional catalyst [1] and is commercially applied as dielectric materials because of its excellent properties [2]. It is also used as a precursor for the synthesis of  $Pb(Zr,Ti)O_3$  (PZT), one important material of several electronic components such as displacement transducers, record player pick-ups, high-frequency filters and actuators [3]. As a precursor, nano-crystalline powders are currently considered to be a suitable particle-size for the solid-state reaction. Besides fineness, the purity and agglomeration of the particles are also important for the fabrication of electronic components. Usual methods for preparing fine  $Zr_xTi_{1-x}O_4$  powders include conventional solid-state reaction [4, 5], co-precipitation [6], sol-gel [7–11] etc. [12]. However, calcination at higher temperature (higher than 650 °C) is necessary in the first two methods for the formation of phase-pure  $Zr_xTi_{1-x}O_4$  powders. These particles are usually extensive agglomerations and exhibit lower reactivity.

There are many papers focusing on the syntheses of complex metal oxides by the hydrothermal method, which is regarded as being superior to other methods for several reasons [13]. This paper shows that the hydrothermal process for the synthesis of  $Zr_xTi_{1-x}O_4$  particles has two advantages: (1) the precipitate derived from the precursor  $Zr_xTi_{1-x}O_2 \cdot nH_2O$  is free from the contamination of ions; (2) the reaction is carried out under moderate conditions.

Yamamoto [14] obtained ZT (53/47) powders by the hydrothermal method, nevertheless, the preparation conditions were not described. We here report the hydrothermal synthesis of a series of  $Zr_xTi_{1-x}O_4$

powders derived from the precursors with compositional changes. The purpose of this paper is to find suitable conditions for preparing the crystalline  $Zr_xTi_{1-x}O_4$  powders and the reaction of  $Zr_xTi_{1-x}O_4$  with PbO is also investigated.

## 2. Experimental

### 2.1. Synthesis

All reagents purchased from Shanghai Co. (People's Republic of China) were of analytical grade and received no further purification before utilization.

Aqueous solution of zirconium nitrate (or zirconium oxychloride) and titanium oxychloride in the requisite Zr/Ti molar ratio of the desired product was dropped into extensive dilute ammonia solution under stirring. The white precipitate  $Zr_xTi_{1-x}O_2 \cdot nH_2O$  was filtered and washed thoroughly by deionized water.

An amount of the precursor  $Zr_xTi_{1-x}O_2 \cdot nH_2O$  was added into deionized water under stirring to form a suspension solution, dilute NaOH or  $HNO_3$  solution was used to adjust the pH if necessary. 16.0 cm<sup>3</sup> of the suspension solution in which the sum of Zr and Ti concentrations was 0.5 mol · dm<sup>-3</sup> was charged into a 20 cm<sup>3</sup> stainless steel autoclave with a Teflon liner. The hydrothermal reaction was conducted at a predetermined temperature for different times. After the autoclave cooling to room temperature, the precipitate was filtered and washed, then dried overnight at ambient temperature.

### 2.2. Reaction of $Zr_xTi_{1-x}O_4$ with PbO

PbO (Orthorhombic) powder with a particle-size of 20–30 nm was obtained by the hydrolysis of  $PbNO_3$

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in ammonia solution. The quantitative oxides PbO and  $Zr_xTi_{1-x}O_4$  in which PbO was more than the required quantity in the desired product by 10% (molar) were crushed in an agate mortar and pelletized under 40 MPa uni-axial power. The PZT's precursor pellet was calcined in a resistance heated muffle furnace at 550, 600, 650 °C with holding periods of 4, 6, 8 h, respectively. After cooling to room temperature in air, the pellet was characterized.

### 2.3. Characterization

The as-prepared products were analyzed by X-ray diffraction (XRD, D/Max-III A) using  $CuK\alpha$  ( $\lambda = 0.15418$  nm) radiation with a nickel filter, graphite monochromator and the crystallinity was calculated with reference to the strongest intensities of all the XRD peaks ( $10\text{--}60^\circ$ ,  $2\theta$ ). A transmission electron microscope (TEM, H-8100IV) was applied to observe the morphology of the crystallites and a plasma spectrometer (ICP-1000) was used to determine the Pb(II), Zr(IV) and Ti(IV) contents in ZT and PZT powders. A Perkin Elmer DTA-1700 differential thermal analyzer was used to obtain the DTA curves and a Perkin Elmer TGA-7 thermogravimetric analyzer the TGA curves ( $10^\circ/\text{min}$ , air atmosphere). BET surface analysis was applied to measure the surface area of the powders.

## 3. Results and discussion

### 3.1. Synthesis of crystalline $Zr_xTi_{1-x}O_4$ powders

#### 3.1.1. Conditions for synthesis of crystalline $Zr_xTi_{1-x}O_4$ powders

Suitable conditions for the synthesis of  $Zr_xTi_{1-x}O_4$  crystallites with a single phase were found by controlling such factors as the homogeneity and composition of the precursor, the pH of the medium and the reaction temperature and time. To find a borderline condition for the formation of  $Zr_xTi_{1-x}O_4$ , the hydrothermal reactions were performed for seven compositions  $x = 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65$  at the predetermined temperatures and held for different times. Fig. 1 shows XRD patterns of the products with the various compositions prepared. The patterns are in agreement with those for  $ZrTiO_4$  [6, 15] and take place with slight peak shifts to greater 2-theta value with  $TiO_2$  content increasing in the product. The patterns also reveal that the crystallinity varies with the compositional change in the precursor.  $ZrTiO_4$  has the greatest crystallinity in the series  $Zr_xTi_{1-x}O_4$ . This result is not in agreement with Cerqueira's [12], in which  $ZrTiO_4$  tends to have the lowest crystallinity under the same conditions.

The pH of the medium usually has an important role on the formation of product in the hydrothermal process [16, 17]. In other words, the effect of pH on the product should not be ignored for any hydrothermal reaction. Table I lists the pH of the medium for the formation of crystalline  $Zr_xTi_{1-x}O_4$  corresponding to the compositional change. The pH range for  $ZrTiO_4$  is the widest.  $ZrTiO_4$  can be prepared in acidic or basic medium. The pH range gradually narrows with the comparative content of Zr and Ti increasing or decreasing.

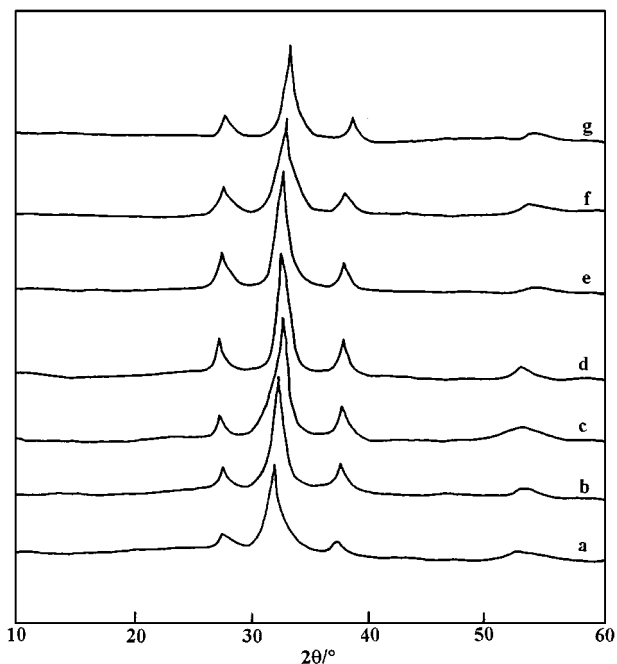


Figure 1 XRD patterns of  $Zr_xTi_{1-x}O_4$  ( $x = 0.35\text{--}0.65$ ) powders derived from various compositional precursors  $Zr_xTi_{1-x}O_2 \cdot nH_2O$ .  $x$ : a. 0.40; b. 0.45; c. 0.50; d. 0.55; e. 0.60. The pH of medium for any reaction is 7.0.

All the crystalline powders can be synthesized in a neutral medium, however,  $Zr_xTi_{1-x}O_4$  rich in  $TiO_2$  precipitates in the slight acidic medium. A higher acidic medium ( $pH \leq 5$ ) might result in the separation of Ti(IV) or Zr(IV) ions and give the anatase  $TiO_2$  or amorphous  $ZrO_2 \cdot xH_2O$  and  $ZrTiO_4$ , whereas the basic medium leads to the precipitation of tetragonal  $ZrO_2$  or anatase  $TiO_2$  and  $ZrTiO_4$ . The above results might be explained as follows: (1) a rapid condensation reaction takes place between  $MO(OH)_2$  groups ( $M = Zr, Ti$ ) [18] in the hydrothermal process, the crystallization of  $ZrO_2$  or  $TiO_2$  starts earlier compared to that of  $Zr_xTi_{1-x}O_4$  and acts as the nucleation for the formation of  $Zr_xTi_{1-x}O_4$  [19]. (2) There are mainly three reversible reactions in this process including the crystallization and dissolution of  $TiO_2$ ,  $ZrO_2$  and  $ZrTiO_4$ ; they compete for chemical species. The products individually depend on the medium while other conditions are held constant. (3) Higher acidity of  $TiO_2$  than that of  $ZrO_2$  is beneficial to the formation of crystalline  $TiO_2$  in the acidic medium [20], whereas the basic medium is favorable to the precipitation of both  $ZrO_2$  and  $TiO_2$ . The formation rate of  $TiO_2$  derived from the precursor stoichiometry rich in  $TiO_2$  is probably faster than that of  $Zr_xTi_{1-x}O_4$  and leads to the precipitation of crystalline  $TiO_2$ , and the precursor stoichiometry rich in  $ZrO_2$  gives amorphous  $ZrO_2$  in the acidic medium. However, both crystalline  $ZrO_2$  and  $TiO_2$  are produced in the basic medium.

For studies on the reaction temperature and time, the crystalline  $Zr_xTi_{1-x}O_4$  ( $x = 0.35, 0.45, 0.50, 0.55, 0.65$ ) powders are prepared at four temperatures 120, 160, 200, 240 °C in neutral mediums, respectively. When the reaction is conducted at 200 °C for 120 h, the precursor stoichiometry rich in  $TiO_2$  or  $ZrO_2$  gives the mixture of  $ZrTiO_4$  and  $TiO_2$  or  $ZrO_2$ . A reaction

TABLE I The pH ranges of the medium for the formation of  $Zr_xTi_{1-x}O_4$  powders

Precursor stoichiometry (Zr/Ti)	Major phases detected from XRD patterns						
	1 <sup>a</sup>	3 <sup>a</sup>	5 <sup>a</sup>	7 <sup>a</sup>	9 <sup>a</sup>	11 <sup>a</sup>	13 <sup>a</sup>
35/65 <sup>b</sup>	A, T	ZT, T	ZT (35/65)	ZT (35/65)	ZT, T	T	T
40/60	A, T	ZT, T	ZT (40/60)	ZT (40/60)	ZT, T	T	T
45/55	T, ZT	ZT (45/55)	ZT (45/55)	ZT (45/55)	ZT (45/55)	ZT, T	T
50/50	ZT, A	ZT	ZT	ZT	ZT	ZT	ZT
55/45	A	ZT, A	ZT (55/45)	ZT (55/45)	ZT (55/45)	ZT (55/45)	ZT, Z
60/40	A	A	ZT, A	ZT (60/40)	ZT (60/40)	ZT, Z	ZT, Z
65/35 <sup>b</sup>	A	A	ZT, A	ZT (65/35)	ZT (65/35)	ZT, Z	ZT, Z

A: amorphous, ZT:  $ZrTiO_4$ , Z: tetragonal  $ZrO_2$ , T: anatase  $TiO_2$ .

<sup>a</sup>pH of the medium.

<sup>b</sup>ZT(35/65) and ZT(65/35) prepared at 240 °C for 240 h, others prepared at 200 °C for 120 h.

temperature higher than 200 °C and time longer than 120 h are necessary for the preparation of the  $Zr_xTi_{1-x}O_4$  crystallites. For example, the hydrothermal reaction must be carried out at 240 °C for 240 h to prepare ZT (35/65) and ZT (65/35) powders. This is not consistent with the solid-state reaction [6], in which  $ZrTiO_4$  is difficult to crystallize compared to other powders. However, it seems to be difficult to crystallize  $Zr_xTi_{1-x}O_4$  stoichiometries rich in  $TiO_2$  or  $ZrO_2$  in the hydrothermal process. This is because the crystallizations of  $TiO_2$  and  $ZrO_2$  are probably faster than those of  $ZrTiO_4$  and the synthesis reaction accelerates with increasing temperature.

$TiO_2 \cdot nH_2O$  and  $ZrO_2 \cdot nH_2O$  were used to prepare  $Zr_xTi_{1-x}O_4$  at 200, 240 °C in a neutral medium to confirm the effect of the compositional homogeneity of precursor on the product. XRD patterns indicated that the phase-pure  $Zr_xTi_{1-x}O_4$  powders were not obtained and the crystalline  $TiO_2$  and  $ZrO_2$  were contained in the product.

Table I also shows that  $Zr_xTi_{1-x}O_4$  stoichiometry rich in  $TiO_2$  or  $ZrO_2$  transforms to  $ZrTiO_4$  and other phases in higher acidic or basic medium. This demonstrates that  $ZrTiO_4$  is the most stable in the series of  $Zr_xTi_{1-x}O_4$  phases. Further, to study the stability of  $Zr_xTi_{1-x}O_4$  under hydrothermal conditions, subsequent experiments were carried out. The as-prepared  $Zr_xTi_{1-x}O_4$  crystallites were added into NaOH or  $HNO_3$  solution (concentrations: 0.1 and  $2.0 \text{ mol} \cdot \text{dm}^{-3}$ ) under stirring to form a suspension solution. The solution was poured into the autoclave, and then heated to 200 °C. The results show that  $Zr_xTi_{1-x}O_4$  powders are stable in dilute  $HNO_3$  or NaOH solution. However,  $Zr_xTi_{1-x}O_4$  stoichiometry rich in  $ZrO_2$  or  $TiO_2$  such as ZT (35/65) or ZT (65/35) transforms to  $ZrTiO_4$  and sodium titanate or tetragonal  $ZrO_2$  in concentrated NaOH solution, whereas  $ZrO_2$  might dissolve  $Zr_xTi_{1-x}O_4$  stoichiometries rich in  $ZrO_2$  to transform  $ZrO_2^{2+}$  in concentrated  $HNO_3$  solution.

### 3.1.2. Influences of some anions

The corresponding sodium salts of  $Ac^-$ ,  $NO_3^-$ ,  $Cl^-$  and  $SO_4^{2-}$  were added to the precursor and the anion concentration controlled at  $0.05 \text{ mol} \cdot \text{dm}^{-3}$ . The hydrothermal reaction was carried at 200 °C for 60, 120, 180, 240 h, respectively. Fig. 2 shows the crystallinity of  $ZrTiO_4$

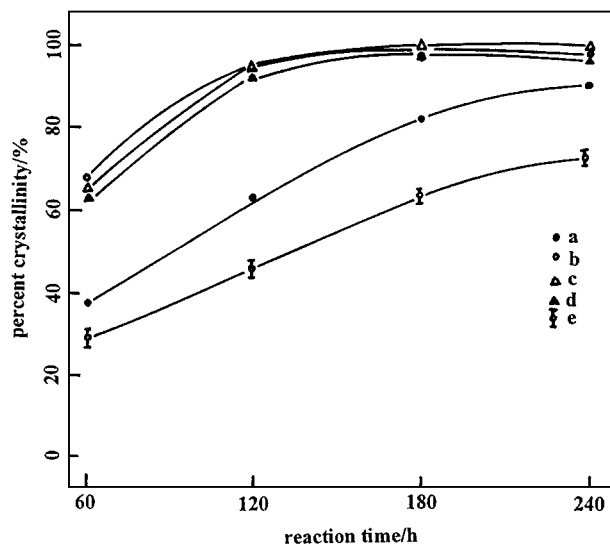


Figure 2 The effects of some anions on the crystallinity of  $Zr_xTi_{1-x}O_4$ . a.  $Cl^-$ ; b.  $Ac^-$ ; c. no anion; d.  $NO_3^-$ ; e.  $SO_4^{2-}$ . Any reaction is carried out at 200 °C and the pH of medium is 7.0.

detected from XRD patterns as a function of reaction time.  $Cl^-$  and  $SO_4^{2-}$  delay the crystallization of  $ZrTiO_4$ , whereas  $Ac^-$  and  $NO_3^-$  do not appear to have any effect on the reaction. XRD patterns also show  $Cl^-$  and  $SO_4^{2-}$  result in the precipitation of  $TiO_2$  derived from the precursor stoichiometry rich in  $TiO_2$ .

### 3.2. Characterization of $Zr_xTi_{1-x}O_4$ powders

Using Scherer's equation, the average particle-size of the powder was calculated from the line broadening of XRD peaks. TEM observations further confirmed that the particles had a mean particle-size of 10–30 nm appearing with a polyhedral morphology and having a simple mode of size-distribution [21]. Fig. 3 shows a representative TEM image of  $Zr_xTi_{1-x}O_4$  particles. It reveals that the powders have a lower agglomeration. Table II lists the surface area of the crystalline  $Zr_xTi_{1-x}O_4$  powders. The high surface area indicates that the powders are very fine and might exhibit high reactivity.

Crystallographic analyses indicate that the structure of  $Zr_xTi_{1-x}O_4$  is orthorhombic with a space group Pnab. The lattice parameters are determined by obtained XRD patterns (scanning rate:  $0.1^\circ/\text{min}$ , using

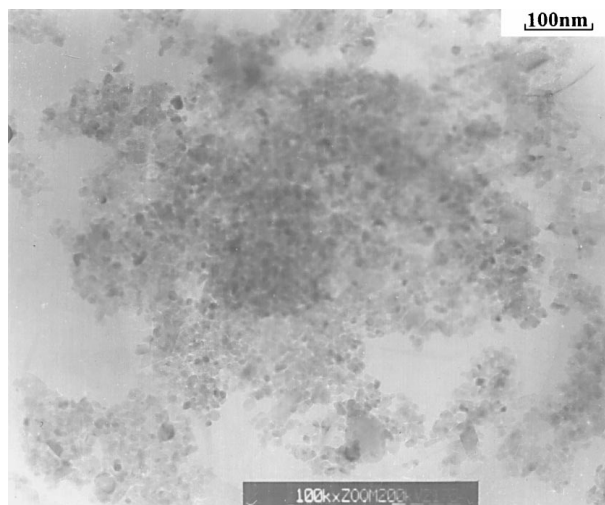


Figure 3 TEM of the ZT (50/50) crystallites. The hydrothermal reaction for preparing this powder is carried out at 200 °C for 120 h.

TABLE II The surface area of crystalline  $Zr_xTi_{1-x}O_4$  powders

Stoichiometry (Zr/Ti) <sup>a</sup>	Crystallinity (%)	Surface area (m <sup>2</sup> · g <sup>-1</sup> )	Ref.
35/65 <sup>b</sup>	92	28.9	—
40/60	100	38.3	—
45/55	100	33.4	—
50/50	100	40.8	9.2 [9], 33.8 [12]
55/45	100	39.2	—
60/40	96	37.8	—
65/35 <sup>b</sup>	96	21.4	—

<sup>a</sup>Based on the ICP results.

<sup>b</sup>Prepared at 240 °C for 240 h, any other powders prepared at 200 °C for 120 h.

TABLE III The lattice parameters of  $Zr_xTi_{1-x}O_4$  detected from X-ray patterns

Stoichiometry (Zr/Ti) <sup>a</sup>	Parameters			Cell volume (nm <sup>3</sup> )
	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)	
35/65 <sup>b</sup>	0.4923	0.5806	0.4740	0.1335
40/60	0.4962	0.5634	0.4792	0.1339
45/55	0.5002	0.5581	0.4814	0.1344
50/50	0.5044	0.5532	0.4837	0.1350
55/45	0.5071	0.5507	0.4862	0.1358
60/40	0.5118	0.5432	0.4900	0.1362
65/35 <sup>b</sup>	0.5162	0.5404	0.4941	0.1378

<sup>a</sup>Based on the ICP results.

<sup>b</sup>Prepared at 240 °C for 240 h, any other powders prepared at 200 °C for 120 h.

KCl as inner standard). The refined lattice parameters are:  $a = 0.5044$ ,  $b = 0.5532$  and  $c = 0.4837$  nm, these values are slight larger than those of  $Zr_xTi_{1-x}O_4$  obtained by quenching after heat-treatment at 1500 °C [15]. Compositional changes result in a significant variation in the cell volume. The corresponding values of lattice parameters for  $Zr_xTi_{1-x}O_4$  are listed in Table III. The parameters  $a$  and  $c$  decrease, parameter  $b$  increases and the cell volume varies from 0.1335 to 0.1378 nm<sup>3</sup> with  $ZrO_2$  content increasing. Compared to the product prepared by the solid-state reaction, the lattice parameters have more significant variation with the compositional change [6].

### 3.3. Reaction of $Zr_xTi_{1-x}O_4$ with PbO

There are many papers on the direct synthesis of PZT including the solid-state reaction [22], sol-gel techniques [23, 24], hydrothermal process [25] and etc [26–28]. Although some methods are not commercially viable, each method has its characteristic features for the preparation of ceramic powder. Thus, as fundamental research, it is essential to investigate the formation process of the product derived from the precursor.

Biggers and many investigators reported the preparation of PZT from PbO, TiO<sub>2</sub> and ZrO<sub>2</sub> by solid-state reaction at temperatures higher than 750 °C [29–31]. However, using  $Zr_xTi_{1-x}O_4$  as the precursor to prepare PZT powders can reduce the laborious cycles of mixture and heating due to the decrease of reactant phases: moreover the process is free of the contamination of possible foreign materials in the product. Yamamoto obtained PZT powders by the use of the reaction of ZT (54/47) with a particle-size of 0.3 μm and PbO at 650 °C [14]. The DTA data for various compositional precursors exhibit two feeble exothermic peaks centered at 530 and 580 °C, respectively, and no distinguishing variation in weight on the corresponding TGA curves, which are assigned to the formation of PbTiO<sub>3</sub> and PZT phases. Besides PbO, the major phases detected from XRD patterns in various products as a function of temperature and period of calcination are listed in Table IV. The formation temperature of phase-pure PZT is as low as 600 °C, which is lower than all the other reported values. One factor is that  $Zr_xTi_{1-x}O_4$  and PbO are nanocrystalline powders, another is that the  $Zr_xTi_{1-x}O_4$  powder might have a high reactivity because of its high surface area and low agglomeration. ICP results

TABLE IV Major phases detected from XRD patterns as a function of temperature and period of calcination

Precursor stoichiometry (Pb:(Zr/Ti))	Major phases detected from XRD patterns								
	550 °C			600 °C			650 °C		
	4 h	6 h	8 h	4 h	6 h	8 h	4 h	6 h	8 h
110:(35/65)	ZT, PT	PT, ZT	PT, PZT, ZT	PT, ZT, PZT	PZT	PZT	PZT	PZT	PZT
110:(40/60)	ZT, PT	PT, ZT	PT, ZT	PT, ZT, PZT	PZT	PZT	PZT	PZT	PZT
110:(45/55)	ZT, PT	PT, ZT	PT, ZT	PT, ZT, PZT	PZT	PZT	PZT	PZT	PZT
110:(50/50)	ZT, PT	PT, ZT	PT, ZT	PT, ZT, PZT	PZT	PZT	PZT	PZT	PZT
110:(55/45)	ZT, PT	PT, ZT	PT, ZT	PT, ZT, PZT	PZT	PZT	PZT	PZT	PZT
110:(60/40)	ZT, PT	PT, ZT	PT, ZT	PT, ZT, PZT	PZT, ZT	PZT	PZT	PZT	PZT
110:(65/35)	ZT, PT	PT, ZT	PT, ZT	PT, ZT, PZT	PZT, ZT	PZT	PZT	PZT	PZT

show that the stoichiometries in the desired products appear no different from those in the precursors within analysis error. It indicates that the desired products have been obtained. XRD patterns also show that the products prepared at 550 °C contain tetragonal  $\text{PbTiO}_3$ .  $\text{Zr}_x\text{Ti}_{1-x}\text{O}_4$  stoichiometry rich in  $\text{TiO}_2$  are favorable to the formation of PZT because the formation of PZT might take place through the intermediate  $\text{PbTiO}_3$  phase [30].

#### 4. Conclusion

Compared to those materials prepared by the conventional solid-state method, the series of  $\text{Zr}_x\text{Ti}_{1-x}\text{O}_4$  crystallites with a mean particle-size of 10–30 nm synthesized hydrothermally appear to exhibit a simple mode of size-distribution. As precursors for preparing PZT powders by the solid-state process they have higher reactivity.

The reaction conditions were varied for formation of products corresponding to different compositions, however, in a neutral medium, all the powders of different compositions can be synthesized at same temperature.

Some anions affected the formation of the product. For example,  $\text{SO}_4^{2-}$  delayed the crystallization of  $\text{Zr}_x\text{Ti}_{1-x}\text{O}_4$  and  $\text{Ac}^-$  appeared to have no distinguishing influence.

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