

# The Effects of pH and Alkaline Earth Ions on the Formation of Nanosized Zirconia Phases Under Hydrothermal Conditions

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## Abstract

The phase composition and crystallite size of zirconia formed under hydrothermal conditions is strongly dependent on crystallization conditions, in particular, pH and a mineralizer. Monoclinic  $ZrO_2$  formed easily in the strong acid and basic media. When  $pH < 1$  or  $> 14$ , monoclinic  $ZrO_2$  was exclusively obtained and its crystallite size increased with increasing pH. In the range of pH 1–14, products of hydrothermal reaction are a mixture of monoclinic and tetragonal  $ZrO_2$ . The effects of  $Mg^{2+}$ ,  $Ca^{2+}$  and  $Sr^{2+}$  ions on the formation of zirconia under hydrothermal conditions were investigated. The presence of these bivalent  $M^{2+}$  ions was in favour of the formation of tetragonal (or cubic)  $ZrO_2$ . The nanosized  $ZrO_2$  crystallites of cubic and tetragonal symmetry were obtained at pH 10, 220°C for 2 h and in the case of  $Ca^{2+}$  and  $Sr^{2+}$  as mineralizer, respectively. © 1999 Elsevier Science Limited. All rights reserved

**Keywords:**  $ZrO_2$ , powders: chemical preparation, hydrothermal methods, X-ray methods, electron microscopy.

## 1 Introduction

The hydrothermal method is a very useful for preparing nanosized zirconia powders. The formation and transformation of zirconia under hydrothermal conditions were exclusively investigated. Mitsuchashi *et al.*<sup>1</sup> found that tetragonal  $ZrO_2$  could not be obtained hydrothermally as the only phase, a small amount of monoclinic  $ZrO_2$  was always present. Nishizawa *et al.*<sup>2</sup> studied

crystallization and transformation of zirconia under hydrothermal conditions and observed that cubic  $ZrO_2$  crystallized at 120°C in concentrated NaOH solutions and abruptly changed into needle-like monoclinic  $ZrO_2$  at 300°C. Tani *et al.*<sup>3</sup> considered that the formation of tetragonal  $ZrO_2$  was closely related to the existence of amorphous zirconia, and the particle size and anionic impurities were not primary factors in stabilization of tetragonal  $ZrO_2$  under hydrothermal conditions. Pyda *et al.*<sup>4</sup> studied the influence of  $Li^+$ ,  $Na^+$  and  $K^+$  ions on hydrothermal crystallization of zirconia and zirconia solid solutions. Adair *et al.*<sup>5</sup> investigated the effect of pH on the formation of monoclinic and tetragonal  $ZrO_2$ . Madsen *et al.*<sup>6</sup> studied the hydrothermal preparation of stabilized zirconia powders. The aim of the present work is to investigate the effects of pH in medium and some bivalent cations ( $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ) on the formation of nanosized zirconia phases under hydrothermal conditions.

## 2 Experimental Procedure

$ZrOCl_2 \cdot 8H_2O$  and  $ZrO(NO_3)_2 \cdot 2H_2O$  were used as starting materials to prepare 0.5 mol  $dm^{-3}$  aqueous solutions. The feedstock was prepared as follows: 40 ml of  $ZrOCl_2$  solution (0.5 mol  $dm^{-3}$ ) and (1.6–8) ml of  $MCl_2$  solution (0.5 mol  $dm^{-3}$ ,  $M = Mg, Ca, Sr$ ) were mixed, KOH solution was used to adjust pH of the mixed solutions at 0.2–14.3, then distilled water added to keep the total volume of the feedstock to 60 ml. The feedstock was charged into a 100 ml Teflon-lined stainless steel autoclave apparatus with electro-magnetic stirrer (Peking University Instrument Factory). The hydrothermal reactions were conducted for 2 h at 220°C. After the autoclave apparatus was cooled to the room temperature in ca 2 h, the produced suspension was

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allowed to stand for 24 h and then after decanting the supernatant it was filtered, washed with acetic acid–ammonium acetate buffer solution and alcohol in order to prevent peptization, and dried at 80°C. The chemical agents used were all analytical reagent grade.

The phase composition of the products was analyzed by X-ray diffractometry (XRD) using Ni-filtered  $\text{CuK}\alpha$  radiation at 40 KV and 100 mA and the scanning rate at  $2^\circ(2\theta) \text{ min}^{-1}$  (diffractometer model Dmax 2400, Rigaku Co, Japan). The diffraction peaks from  $2\theta = 72$  to  $76^\circ$  were used to distinguish between the tetragonal and cubic  $\text{ZrO}_2$  phase.<sup>2</sup> The morphology of the products was observed using transmission electro microscopy (TEM) (model JEM-200CX, JEOL Ltd., Japan). Particle size distributions were determined using the X-ray small angle scattering method. The average crystallite size was calculated from the (111) diffraction peak using the Scherrer formula ( $D = 0.9\lambda / \beta \cos \theta$ ). The content of tetragonal (or cubic)  $\text{ZrO}_2$  in the products was qualitatively estimated from the

relative intensities of the (111) peaks of tetragonal (or cubic) and monoclinic  $\text{ZrO}_2$ .

### 3 Results and Discussion

#### 3.1 Effect of pH

The pH of the reaction medium has obvious effects on the hydrolysis of metal ions. According to the charge versus pH diagram taken from Kepert,<sup>7</sup> the hydrolysis of  $\text{Zr}^{4+}$  ions yields aquo( $-\text{OH}_2$ ), aquo-hydroxo( $-\text{OH}$ ), hydroxo, hydroxo-oxo( $=\text{O}$ ) or oxo complexes with increasing pH in aqueous media. The polycations,  $[\text{Zr}_4(\text{OH})_8(\text{OH}_2)_{16}]^{8+}$ , form via olation in low-pH media. In this case, no precipitate appears even though the  $\text{ZrOCl}_2$  solution was heated to boil. Under hydrothermal conditions, further hydrolysis of the terminal aquo-ligands resulted in condensation yielding small spherical  $\text{ZrO}_2$  particles mainly of monoclinic structure [Fig. 1(a) and (b)]. An aggregation occurred between small  $\text{ZrO}_2$  particles due to the large surface energy.

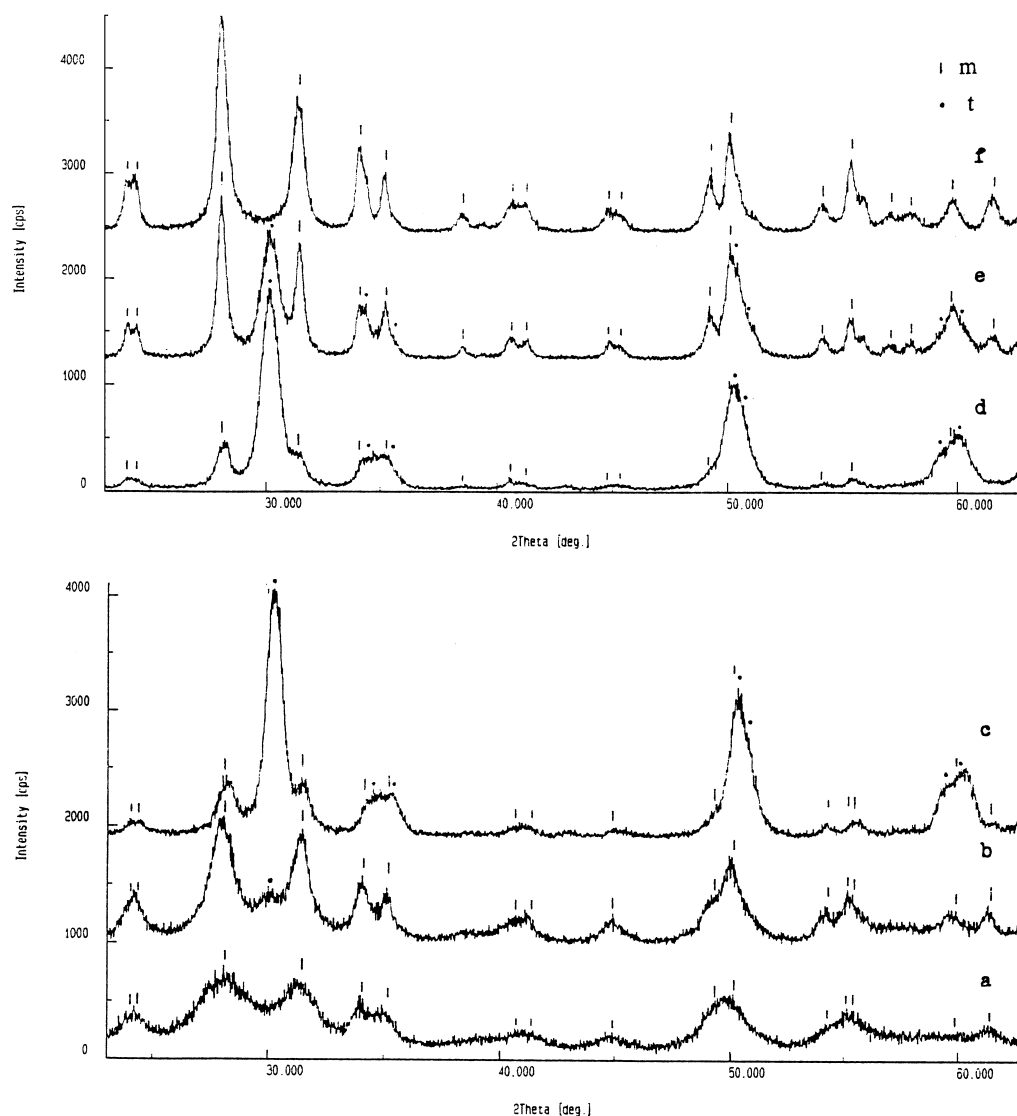


Fig. 1. XRD patterns of products formed at pH: (a) 0.8; (b) 2.7; (c) 6.5; (d) 10.2; (e) 12.0 (f) > 14.

This resulted in chainlike aggregates which formed spindle agglomerates [Fig. 2(a) and (b)].

In the range of pH 1~14, the powders were the mixture of monoclinic and tetragonal  $ZrO_2$  phase which predominated in the products as  $6 < \text{pH} < 10$  [Fig. 1(c)–(e)]. It seems that the hydroxo(–OH) complex as the precursor is in favour of the formation of tetragonal  $ZrO_2$  under hydrothermal conditions. However, the tetragonal phase as the only one is not obtained and this result is consistent with Ref. 1. At  $\text{pH} < 10$ , the particle sizes

of monoclinic and tetragonal  $ZrO_2$  were smaller than 10 nm [Fig. 2(c) and (d)]. At  $\text{pH} > 10$ , monoclinic  $ZrO_2$  particles grew remarkably from 8 to 40 nm (relative XRD peaks narrowed) while those of tetragonal symmetry kept unchanged (8 nm). The tetragonal phase converted gradually into the monoclinic symmetry with increasing pH most probably by aggregation and recrystallization [Fig. 1(e)].

At  $\text{pH} \geq 14$ , the monoclinic  $ZrO_2$  phase of rod-like shape [Fig. 2(f)] and the size of  $30 \times 80$  nm was

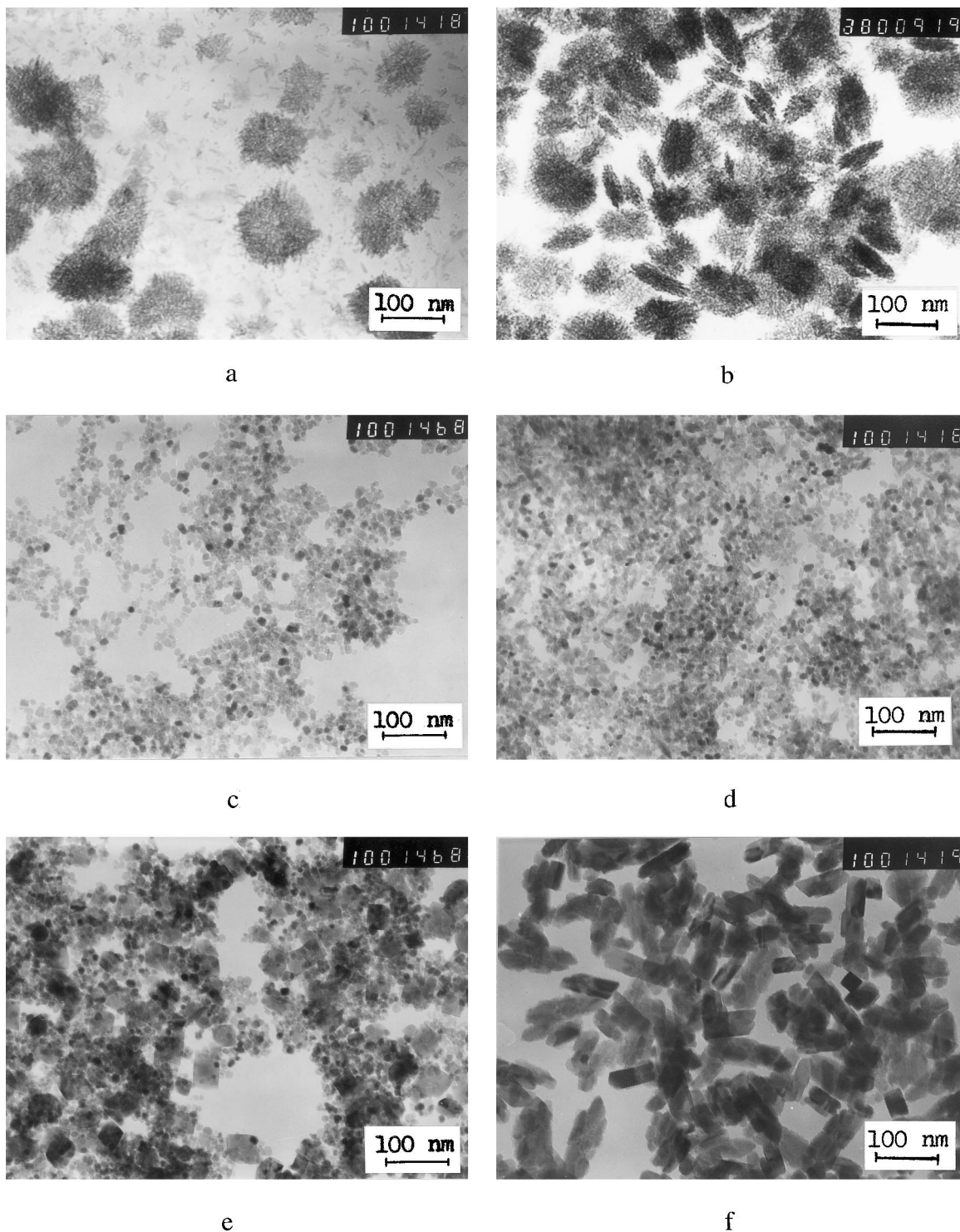
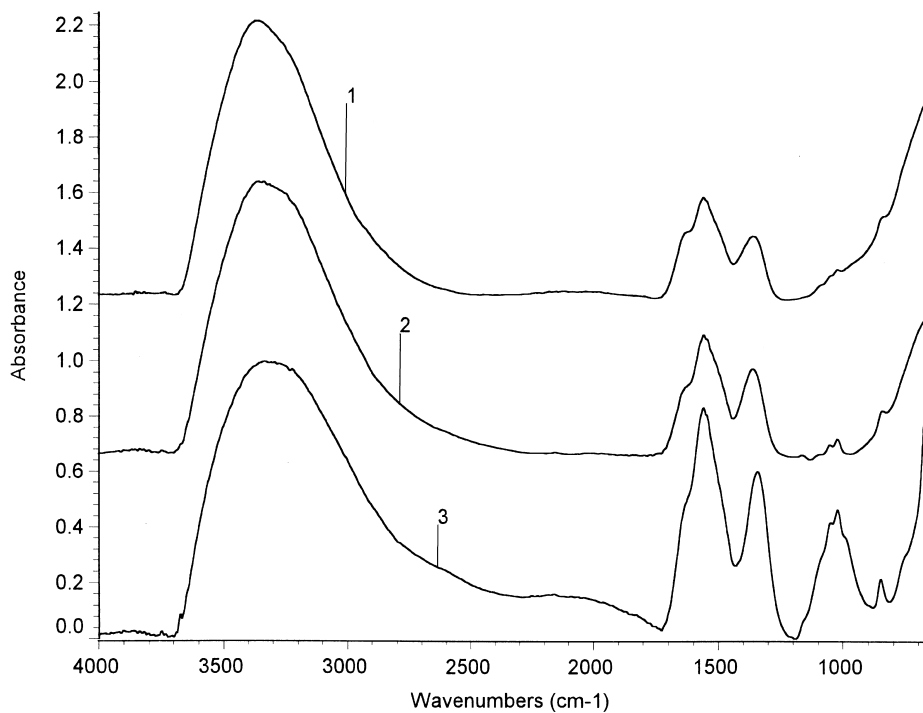
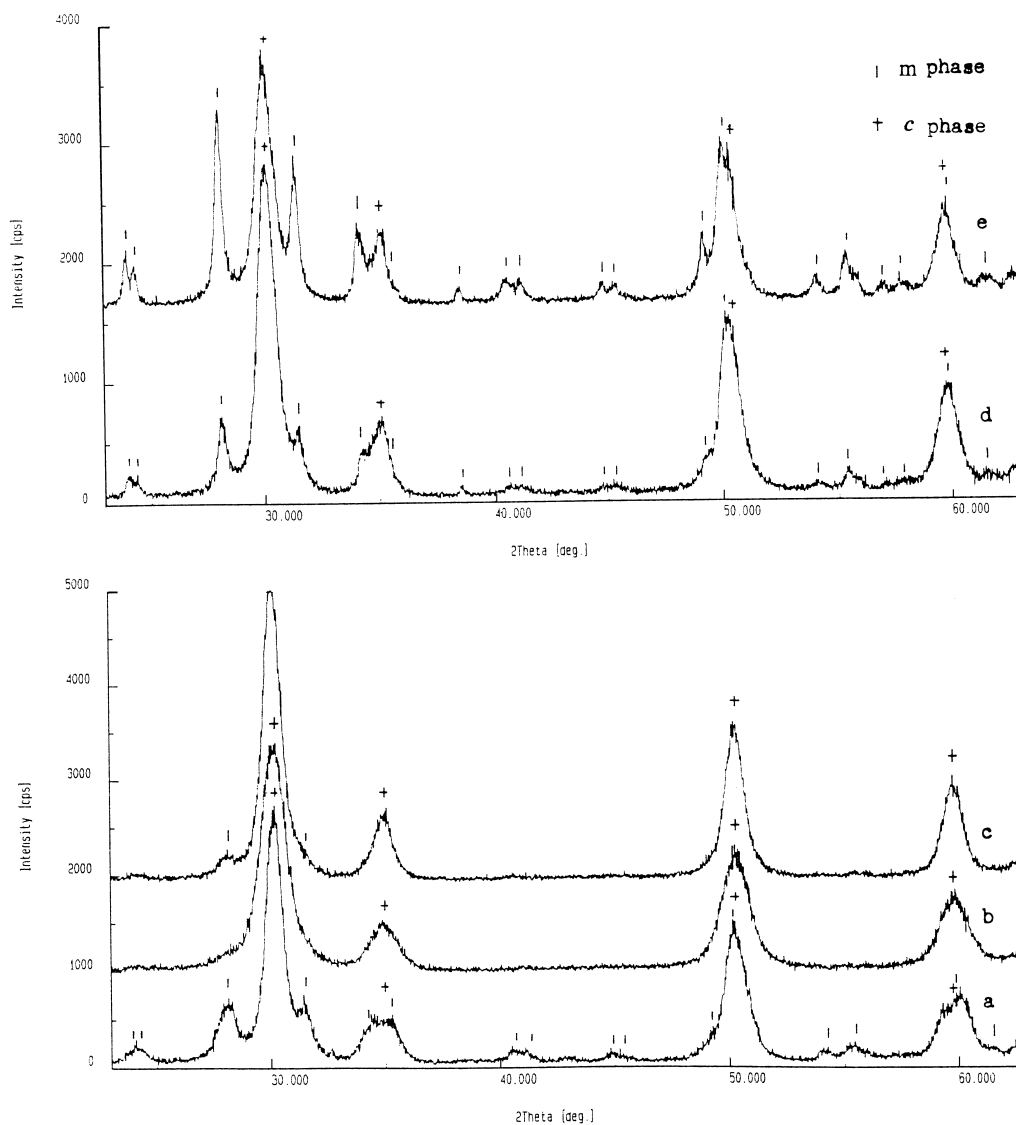


Fig. 2. TEM micrographs of products formed at pH: (a) 0.8; (b) 2.7; (c) 6.5; (d) 10.2; (e) 12.0; (f) > 14.



**Fig. 3.** IR spectra of precursors formed at: (1) pH 10.02; (2) pH 10.02, with 8 mol% Ca<sup>2+</sup>; (3) pH 14.03.



**Fig. 4.** XRD patterns of products (with 8 mol% CaCl<sub>2</sub>) formed at pH: (a) 6.0; (b) 10.0; (c) 11.8; (d) 13.5; (e) 14.0.

obtained most probably due to strong recrystallization and aggregation under hydrothermal conditions [Fig. 1(f)].

The effects of pH on the phase composition of the product are closely connected to effects of pH on the structure of hydrous oxide precursor. IR spectra of the precursors (hydrous zirconia gels which were filtered, washed by deionized water and dried at 80°C) formed in different conditions are shown in Fig. 3. The absorption peak at  $\sim 3300\text{ cm}^{-1}$  broadens with increasing pH from 10.02 to 14.03 [Fig. 3(1)–(3)] indicating the increased association of OH ligands in hydrolytic products for  $\text{Zr}^{4+}$  ions. The differences in structure of the precursors give rise to different condensation-linking manners under hydrothermal conditions and as a result, to forming  $\text{ZrO}_2$  of different symmetry. The absorption peaks in the range of  $800\sim 1700\text{ cm}^{-1}$  are the characteristic peaks of

$\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  groups which formed because of  $\text{CO}_2$  absorbed by the gels from the air.<sup>8</sup>

### 3.2 Effect of bivalent cations

The mineralizer has an important influence on the formation of different zirconia phases under hydrothermal conditions.

#### 3.2.1 $\text{CaCl}_2$ as mineralizer

Figure 4 shows the XRD patterns of products formed by adding 8 mol%  $\text{CaCl}_2$  to  $\text{ZrOCl}_2$  water solution at different pH media. For comparison, the XRD patterns (from  $2\theta=70$  to  $76^\circ$ ) of the products obtained in the absence and presence of  $\text{Ca}^{2+}$  ions at  $\text{pH}\sim 10$  are shown in Fig. 5(a) and (b), respectively. Analyzing the line at  $2\theta=73.96^\circ$ , it can be affirmed that  $\text{ZrO}_2$  formed in presence of  $\text{Ca}^{2+}$  is cubic symmetry with  $a=0.5126\text{ nm}$  (calculated by least square method), which is slightly more than that in Ref. 2 ( $a=0.5119\text{ nm}$ ). From Figs 4 and 5, it can be seen that only cubic  $\text{ZrO}_2$  was obtained at  $\text{pH}\sim 10$  using  $\text{CaCl}_2$  as the mineralizer. The TEM micrograph in Fig. 6(a) shows the morphology of the cubic  $\text{ZrO}_2$  powder. The particle size distribution of cubic  $\text{ZrO}_2$  obtained by the X-ray small angle scattering method shown in Fig. 7 indicates that 88% crystallites were smaller than 10 nm.

Comparison of IR spectra of hydrous oxide precursors for  $\text{Zr}^{4+}$  species in the absence [Fig. 3(1)] and presence [Fig. 3(2)] of  $\text{CaCl}_2$  at  $\text{pH}\sim 10$  revealed that addition of  $\text{CaCl}_2$  broadened absorption peak at  $\sim 3300\text{ cm}^{-1}$ . It could be due to the fact that  $\text{Ca}^{2+}$  species were adsorbed on the surface of precursor particles changing the association of OH ligands in the precursors.

The other important effects of Ca-additive were a decrease in particle size and delay of the conversion of  $\text{ZrO}_2$  (cubic or tetragonal) to monoclinic form. The average particle size of cubic  $\text{ZrO}_2$  was ca 7 nm [Figs 4(b) and 6], and was smaller than

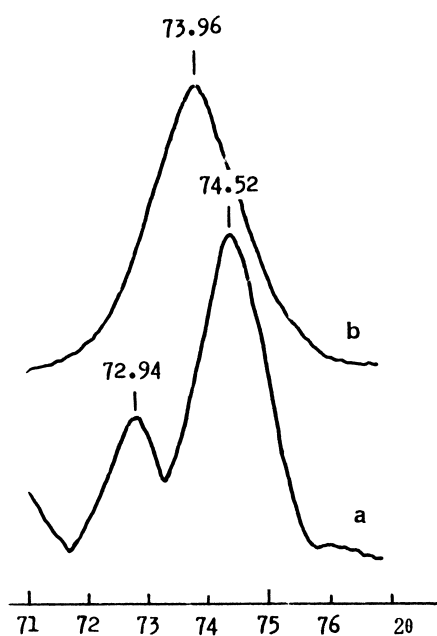


Fig. 5. XRD patterns of products without (a) and with  $\text{CaCl}_2$  (b) from  $2\theta=71$  to  $76^\circ$  at  $\text{pH}\sim 10$ .

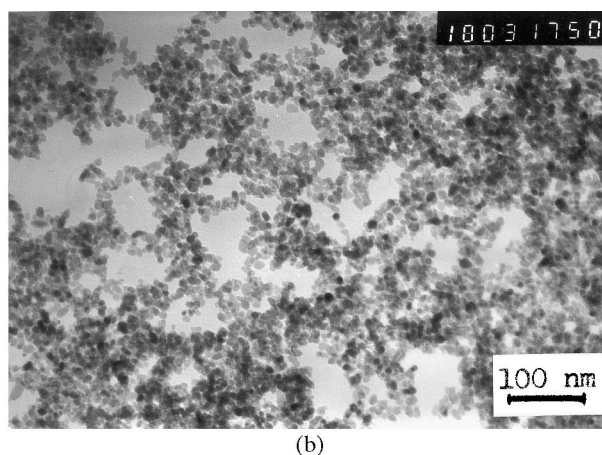
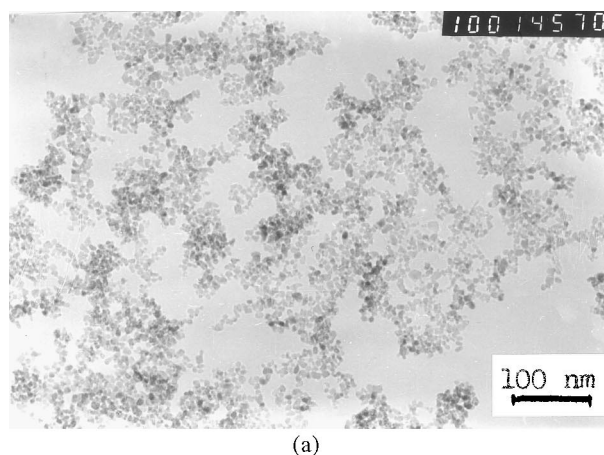


Fig. 6. TEM micrographs of (a)  $\text{ZrO}_2$ (c) (with 8 mol%  $\text{CaCl}_2$ ) and (b)  $\text{ZrO}_2$ (t) (with 8 mol%  $\text{SrCl}_2$ ).

that formed in the Ca-free case. Measure the monoclinic  $ZrO_2$ /tetragonal  $ZrO_2$  ratio qualitatively, it was already  $> 1$  at pH  $\sim 12$  in Ca-free case, but this ratio was still  $< 1$  at pH  $\sim 14$  in the Ca-adding case. By changing the amount of  $CaCl_2$  from 4 to

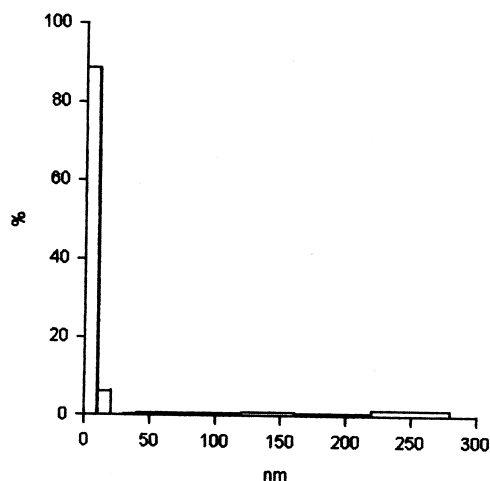


Fig. 7. Distribution of particle size (weight mean diameter) for  $ZrO_2$  (c) sample.

20 mol%, the cubic  $ZrO_2$  phase as the predominant one can be obtained at pH  $\sim 10$ , and with increasing Ca-additive, the average grain size tended to decrease (relevant XRD peaks broadened), but the cell parameters unchanged, for example, the  $2\theta_{(311)}$  of the samples are all equal to  $59.85^\circ$ . The ionic radii of  $Ca^{2+}$  and  $Zr^{4+}$  were 114 and 92 pm, respectively.<sup>9</sup> If  $Ca^{2+}$  is substituted for  $Zr^{4+}$  in cubic  $ZrO_2$ , the lattice parameters must be increased with increasing amount of  $CaCl_2$ . The lack of cell parameter changes indicates that most of the  $Ca^{2+}$  ions did not enter the lattice of cubic  $ZrO_2$  to substitute  $Zr^{4+}$  ions. They probably were absorbed on the surface of  $ZrO_2$  crystallites, preventing their growth and providing the environment which favored the formation of cubic  $ZrO_2$ . Using  $1.6 \times 10^{-4} \text{ mol dm}^{-3}$   $CaCl_2$  solution as the reference, the rate of recovery for  $CaCl_2$  is near 100% with ICP method (Inductively Coupled Plasma Emission Spectrometry). The amount of  $Ca^{2+}$  ions in the mother liquor after hydrothermal reaction is only ca 0.5% of the adding  $Ca^{2+}$  amount in the

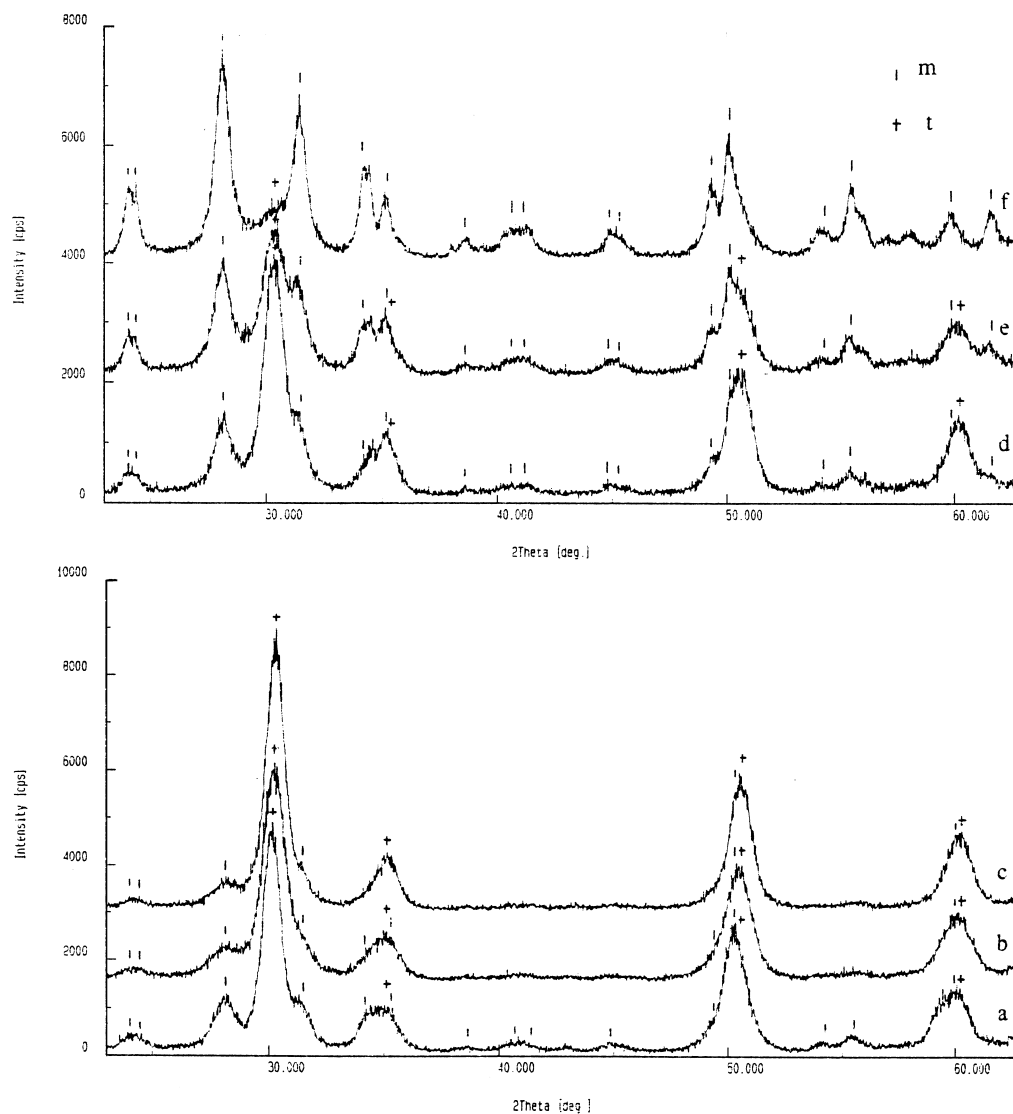


Fig. 8. XRD patterns of products (with 8 mol%  $MgCl_2$ ) formed at pH: (a) 6.6; (b) 9.3; (c) 10.1; (d) 11.6; (e) 13.1; (f) 13.9.

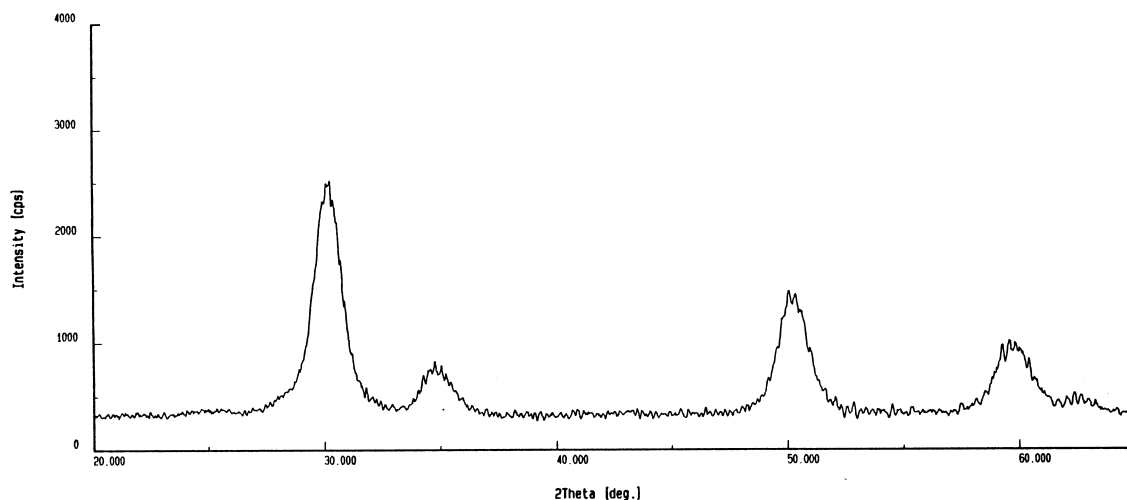


Fig. 9. XRD pattern of product (with 8 mol% SrCl<sub>2</sub>) formed at pH~10.

case of adding 8 mol% CaCl<sub>2</sub>. The above results confirm the supposition that Ca<sup>2+</sup> ion did not incorporate into the lattice of cubic ZrO<sub>2</sub> and probably was adsorbed on the surface of ZrO<sub>2</sub> crystallites at the applied conditions of hydrothermal treatment. CaCl<sub>2</sub> may play the role of mineralizer under hydrothermal conditions.

### 3.2.2 MgCl<sub>2</sub> and SrCl<sub>2</sub> as mineralizer

The influence of MgCl<sub>2</sub> and SrCl<sub>2</sub> as mineralizer on the formation of ZrO<sub>2</sub> phases was also examined. The XRD patterns of products formed by adding 8 mol% MgCl<sub>2</sub> to ZrOCl<sub>2</sub> water solution at different pH media are shown in Fig. 8. They indicate that the products were the mixture of monoclinic ZrO<sub>2</sub> and tetragonal or cubic ZrO<sub>2</sub>. The monophase ZrO<sub>2</sub> powder was not obtained under applied experimental conditions. However, the presence of Mg<sup>2+</sup> ions seems to favour the formation of tetragonal ZrO<sub>2</sub> [compare with Figs 1(e) and 8(e)].

SrCl<sub>2</sub> as the mineralizer has not been investigated systematically, but the tetragonal ZrO<sub>2</sub> phase was obtained with adding 8 mol% SrCl<sub>2</sub> at pH~10. Figure 9 shows its XRD pattern. Two diffraction peaks can be observed in the range of 71–76°. The morphology of the powder is shown in Fig. 6(b). It was uniform and nanosized similarly to the powder crystallized without the mineralizer at pH~10 [Fig. 2(d)].

## 4 Conclusion

The nanosized powders composed of monoclinic, tetragonal and cubic ZrO<sub>2</sub> or their mixtures have been prepared under hydrothermal conditions. pH and the mineralizer have significant effect on the phase composition of the zirconia powders. The monoclinic ZrO<sub>2</sub> formed easily at very low (< 1) and very high (> 14) pH. The nanosized cubic ZrO<sub>2</sub> is

formed in the presence of Ca<sup>2+</sup> as the mineralizer at pH~10. The nanosized tetragonal ZrO<sub>2</sub> is prepared in the presence of Sr<sup>2+</sup> as mineralizer at pH~10. The reason that zirconia phases of different symmetry are formed under hydrothermal conditions could be concerned with coordinational situations around Zr ions in the precursor. The relevant mechanism is being studied.

## Acknowledgements

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