ELSEVIER

Ceramics International 30 (2004) 469–475

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Preparation and characterization of a novel zirconia precursor

Gong-Yi Guo[a,*], Yu-Li Chen[b]

[a]*Department of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200030, China*
[b]*College of Chemistry and Chemical Engineering, Shanghai University, Shanghai 200072, China*

Received 15 April 2003; received in revised form 5 May 2003; accepted 16 June 2003

Abstract

A novel zirconium oxy-hydroxy-acetate was synthesized from zirconium oxychloride and acetic acid solution by a simple metalorganic precipitation process. On the basis of differential thermal, thermogravimetric, and elemental analyses of the precipitation complex, it could be described as $Zr_4O_3(OH)_7(CH_3COO)_3{\cdot}5H_2O$, which was further confirmed by its infrared spectra and X-ray diffraction measurements. A tentative assignment was made for each band in the infrared spectrum of the zirconium-oxy-hydroxy-acetate, and the assignments discordant with those in the literature proposed for some bands. The structure development in the precipitating complex and its pyrolysis products was investigated as a function of the heat processing temperatures, showing that the zirconium oxy-hydroxy-acetate could yield a zirconia comparable to that formed from zirconium acetate solution by the other processes in the literature. The present process offers distinct advantages in terms of time- and energy-saving and environmental friendliness.

© 2003 Elsevier Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Precursor; B. Spectroscopy; B. X-ray methods; C. Thermal properties; D. Zirconia

1. Introduction

Zirconia and zirconia-based ceramics are of both scientific and technological interest as structural and functional materials due to their superior properties such as: excellent refractance and chemical resistance, good mechanical strength, high fracture toughness and hardness, large ionic conductivity, low thermal conductivity at high temperature, and good thermal stability and resistance to thermal shock. During the last decades an active research has been undertaken in different laboratories, in order to obtain zirconia and zirconia-based ceramic powders with the required characteristics of size, purity, uniformity, crystallinity etc. As a result of the intensive work done, a wide variety of physical and chemical preparation techniques were found. Among them there was a zirconium acetate precursor route. In the literature the zirconium acetate was prepared by the reaction of zirconium chloride with excess of pure acetic acid below 80 °C under reduced pressure. If the reactants were allowed to reflux at their boiling points, then the product obtained was zirconium oxyacetate or a mixture of tetraacetate and oxyacetate [1,2]. The synthesis of a zirconium oxy-(or oxy-hydroxy)-acetate was done by dissolving a small amount of zirconium oxychloride or carbonate in a heavy excess of boiling pure acetic acid, evaporating the resulting solution to a definite volume, and then cooling and allowing it to stand for 12 h. The zirconium oxyacetate or the zirconium oxy-hydroxy-acetate prepared in this way was characterized as $Zr_4O_3(CH_3COO)_{10}{\cdot}3H_2O$ or $Zr_2O(OH)(CH_3COO)_5{\cdot}2H_2O$[3]. In this work we have developed a simple metalorganic precipitation process to obtain a zirconium oxy-hydroxy-acetate with the composition and structure significantly different from those previously known. In addition, only by calcining the zirconium oxy-hydroxy-acetate $Zr_4O_3(OH)_7\ (CH_3COO)_3\ {\cdot}5H_2O$ a comparable zirconia can be produced to that formed from zirconium acetate solution either by desiccation and pyrolysis [4,5], by boiling under reflux [6] or by hydrolysis, drying and pyrolysis [7].

2. Experimental

2.1. Materials

Pure acetic acid (>99%), analytical reagent-grade ammonia and zirconium oxychloride octahydrate were

---

* Corresponding author. Fax: +86-21-64319501.

0272-8842/$30.00 © 2003 Elsevier Ltd and Techna S.r.l. All rights reserved.
doi:10.1016/S0272-8842(03)00133-0

obtained from Shanghai Chemical Reagent Plant and used as received.

2.2. Synthesis

To 100 ml of 2.6 wt.% acetic acid solution was dropwise added 5 ml of zirconyl chloride solution (Zr 38.76 g 1^{-1}) followed by concentrated aqueous ammonia with constant stirring. At pH 5.0 a white turbidity appeared. When the pH value approached to 5.8, a significant turbidity was developed. The resultant precipitate (a zirconium acetate-complex) was aged for 2 days until the supernatant became nearly clear, filtered, washed with deionized water thoroughly, and dried at 70 °C for 56 h in order to make chemical analyses and physical measurements. The resulting xerogel looked yellowish.

2.3. Analyses and measurements

The zirconium in the zirconyl chloride solution, and in the dried precipitate, i.e., xerogel also called precursor, was assayed by inductively coupled plasma-atomic emission spectroscopy using a IRIS Advantage/1000 ICP-AES spectrophotometer (Thermo Jarrel Ash Corporation, USA). The determination of carbon, hydrogen, nitrogen, and oxygen in the xerogel and its pyrolysis products was made by a Perkin Elmer SeriesII CHNS/O Analyzer 2400, USA, and the determination of chlorine by combustion process using KLY Halogen Microcoulombmeter, China. The detection limits were 0.3% for carbon, hydrogen, nitrogen, and oxygen, and 0.5% for chlorine, respectively.

Fourier transform infrared spectra for pure acetic acid and for the xerogel and its pyrolysis products were recorded on a Bruker Equinox 55 spectrophotometer in wavenumber 4000–400 cm^{-1} range, with a resolution of 4 cm^{-1} and a scan number of 25. The infrared spectra of the pure acetic acid, xerogel and its pyrolysis products were studied by putting a droplet of the acid between two ZnSe windows, and as powder dispersed in a KBr pellet, respectively.

The xerogel was examined by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) with a thermal analyzer (Universal V2. 4F TA Instruments, USA). These experiments were conducted up to 800 °C with a heating rate of 10 °C min^{-1} in air.

A Bruker-AXS D8 Advance diffractometer (Germany) was used to collect X-ray diffraction (XRD) data for the structural analysis of the xerogel and its pyrolysis products derived from its thermal treatment at different temperatures. The samples were scanned over a 2θ range of 20–90°at a scanspeed of 0.2 sec/step with an increment 0.02°/step using CuK_α radiation at 40 kV and 40 mA. The identification and quantitation of monoclinic (M), tetragonal (T) and cubic (C) zirconia were accomplished by comparison of the XRD data to the Powder Diffraction File according to the relationships used by us previously [8,9]. The amount of tetragonal phase(T) present in a powder is estimated from the following relationship:

$$T = \frac{\frac{1}{4} I_{\mathrm{t}(200)}}{\frac{1}{4} I_{\mathrm{t}(200)} + \frac{1}{6} I_{\mathrm{c}(200)}}$$

where $I_{\mathrm{t}(200)}$is the intensity of the tetragonal peak (200)and $I_{\mathrm{c}(200)}$ indicates the intensity of the cubic peak (200). The amount of monoclinic phase (M) present in a powder is calculated from the following relationship:

$$M = \frac{I_{\mathrm{m}(111)}}{I_{\mathrm{m}(111)} + I_{\mathrm{t}(111)} + \frac{1}{8} I_{\mathrm{c}(111)}}$$

Where $I_{\mathrm{m}(111)}$ denotes the intensity of the monoclinic peak (111), $I_{\mathrm{t}(111)}$ refers to the intensity of the tetragonal peak (111) and $I_{\mathrm{C}(111)}$ represents the intensity of the cubic peak (111). The crystallite sizes of the crystalline pyrolysis products were estimated by applying the well-known Scherrer equation to the half-height widths of reflections selected from the XRD patterns.

3. Results and discussion

3.1. Infrared features

The structure of the zirconium acetate-complex synthesized in this way can be identified on the basis of its infrared spectra, X-ray diffraction, thermal and elementary analyses data. In order to make the infrared assignments for the zirconium acetate-complex more reliable we have compared the infrared spectrum of the zirconium acetate-complex with that of acetic acid. Fig. 1 presents the infrared spectrum of acetic acid, showing the following characteristic bands: O–H stretching around 3053 cm^{-1}, C=O stretching around 1714 cm^{-1}, $\mathrm{CH_3}$ bending and C–O–H bending around 1413 cm^{-1}, C–O stretching and C–O–H bending around

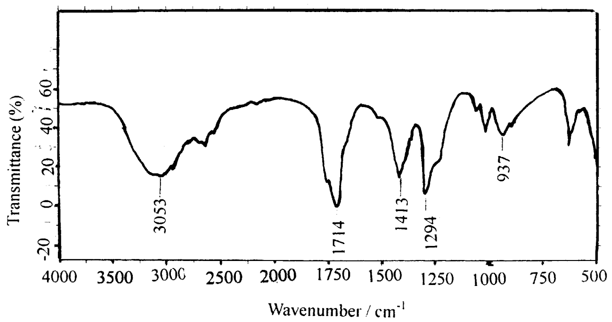

Fig. 1. IR spectrum of acetic acid.

1294 cm^{-1}, the out-of-plane bending of the bonded O–H around 937 cm^{-1} [10–15]. Fig. 2 exhibits the infrared spectrum of the zirconium acetate-complex. It is well accepted that the most significant information about the mode of coordination of carboxylic acids can be obtained from the analysis of characteristic frequencies of carboxyl groups. In the infrared spectrum the band at 3422 cm^{-1} is due to the –OH stretching vibration in the acetate molecule. The bands around 1562 and 1422 cm^{-1} are attributed to the asymmetric and symmetric stretching vibrations of the carboxyl (–COO^-) for the acetate ion, respectively. The frequency separation between the asymmetric and symmetric carboxyl stretching vibrations of an acetate group is an indication of the coordination mode of the acetate ion coordinated to a metal cation. In general, a bridging bidentate carboxylate exhibits a $\Delta \upsilon$ value on the order of the free ionic value of ~160 cm^{-1}. For a chelating carboxylate the value of $\Delta \upsilon$ is less than 100 cm^{-1}, while unidentate coordination results in $\Delta \upsilon$ value greater than 200 cm^{-1} [16,17]. In the present case, the frequency separation is 140 cm^{-1}, suggesting that the infrared spectrum for the zirconium acetate-complex exhibits the bands corresponding to the bridging bidentate acetate ligand.

The infrared spectra of some known zirconium acetates [1] and oxy-hydroxy-acetates [3] did not contain any intense band in the stretching frequency region (900–1100 cm^{-1}) of most of the metal-oxygen double bonds [18], thereby indicating the absence of zirconyl group Zr=O in these acetates. While Geiculescu et al. have observed the bands at 957, 1026 and 1055 cm^{-1} for the zirconium acetate gel containing NO_3^- ions [19], and associated the bands with the presence of double bonds of zirconyl groups Zr=O in the zirconium acetates, we presume that the bands may be related to the presence of nitrogen rather than to the presence of Z_r =O bond in their zirconium acetate gel, because nitrogen has a similar atomic weight to that of oxygen, which might give rise to a similar frequency [18]. Also, the infrared spectrum of the zirconium acetate-complex under investigation exhibits a well-defined band at 1026 cm^{-1} that falls within this region (900–1100 cm^{-1}), but we ascribe the band to CH_3 rocking rather than the zirconyl group (Zr=O), in line with the assignment on zirconium acetates and related compounds [10,17,20,21]. Further, such an assignment of the band can be supported by taking into consideration that the previous paper that reported the stretching frequencies of metal-oxygen double bonds did not deal with zirconium [18] and that several published works on some zirconium compounds have shown that the stretching frequencies of the Zr=O bond appear at 877 cm^{-1} [22,23] and around 780 cm^{-1} [24,25].

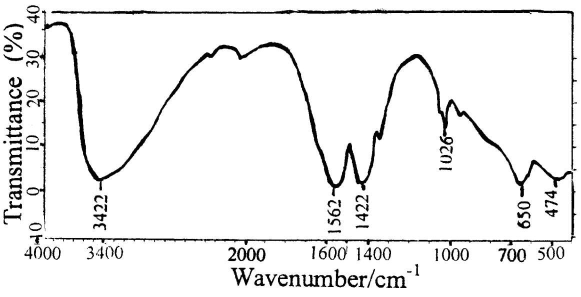

Fig. 2. IR spectrum of zirconium acetate-complex $Zr_4O_3(OH)_7(CH_3COO)_3{\cdot}5H_2O$.

Finally, it may be noted by comparing Fig. 1 with Fig. 2 that two new bands at 650 and 474 cm^{-1} obviously emerges in the infrared spectrum of the zirconium acetate-complex. On the basis of the infrared band assignments of zirconium acetate [1,21], oxy-hydroxy acetate [20], related carboxylates [26], oxychloride [27], zirconia [8,28], and other metal carboxylates [10,17,29,30], we associate the two bands with a deformation mode of acetate group and with Zr–O stretching vibrations, respectively. Overall, it can be assumed from the presence of these infrared bands that the precipitating complex is a basic zirconium acetate-complex in which an acetate ion is directly bonded to the zirconium of tetramer $[Zr_4(OH)_8]^{8+}$ mainly in a bridging bidentate coordination mode and the resulting tetramers are linked together by the acetate ions or OH bridges.

3.2. Thermal behaviour

Investigation of the behaviour of thermal decomposition of the xerogel may lead to clarification of the composition of the precipitating complex prepared by the present process. Thermogravimetric (TGA), differential thermal (DTA) and elemental analyses were used to obtain information about the decomposition behaviour of the xerogel when it was heated in air.

When the basic zirconium acetate-complex was heated up to 800 °C in air, the TGA and DTA traces are shown in Fig. 3. It can be seen that a one-to-one correlation exists between the DTA and TGA traces, indicating that the thermal effects are accompanied by weight losses. The thermal decomposition proceeds in three steps for the complex. An endothermic peak at 119 °C originates from the dehydration of the dried precipitating complex, i.e., xerogel. The weight loss of 10.95% observed from the TGA curve arises from the dehydration. After the dehydration there are two exothermic peaks at about 396 and 545 °C, and the corresponding weight losses are 17.38 and 10.19%, respectively, suggesting that the major fraction of the precipitating complex should be decomposed in the first exothermic step. In addition, the TGA curve shows that a gradual weight loss of the xerogel goes up to 710 °C, no variation of weight is found above this temperature, and at 710 °C the initial weight of 61.48% is present in the final stage as a white powder, attributed to zirconia. In order to determine the assignments of the two exothermic peaks, we have used X-ray diffraction, infrared spectroscopy and elemental analyses to follow the structural modification of the precipitating complex with the thermal evolution of it.

Figs. 4 and 5 show the X-ray diffraction patterns and infrared spectra of the xerogel and its pyrolysis products obtained by heating it at the temperatures 396, 545 and 710 °C corresponding to the exothermic and the final stages in the DTA and TGA curves. The as-prepared xerogel is amorphous to XRD. The infrared spectrum (Fig. 5a) of the xerogel displays the characteristic infrared bands of the acetate at 3422, 1562, 1422, 650 and 474 cm^{-1}. Their assignments have been, in detail, discussed in the above section. The intensities of these bands are significantly reduced in the infrared spectrum (Fig. 5b) of the product obtained by heating the xerogel at 396 °C, suggesting that most of the precipitating complex has been decomposed at 396 °C. This result is in good agreement with that from the above-mentioned thermal analysis, and supported by elemental analyses. Elemental analyses reveal that the carbon and hydrogen contents in the product derived from the first exothermic step is much lower than those in the xerogel (Table 1), indicating that the major fraction of the precipitating complex has been decomposed in the first exothermic step. In addition, the product derived from the first exothermic step has been detected by X-ray diffraction to be a mixture of cubic and tetragonal zirconia (Fig. 4b), in which the cubic and tetragonal phases account for 66 and 34%, respectively. Therefore, the

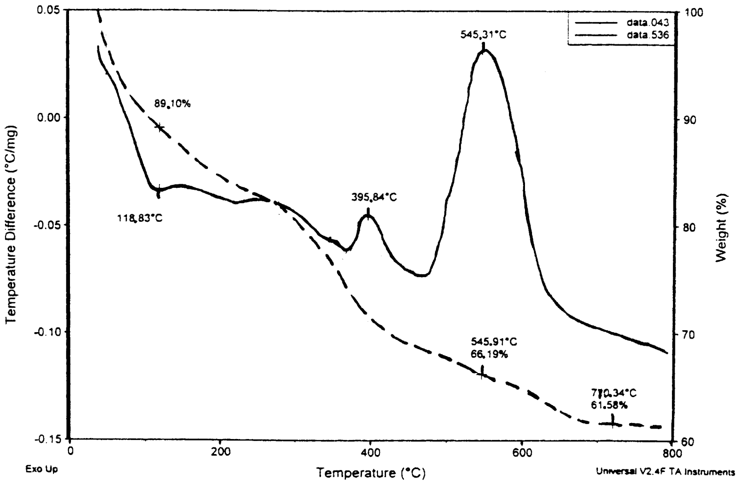

Fig. 3. DTA and TGA curves of the zirconium acetate-complex (DTA, solid line; TGA, dashed line).

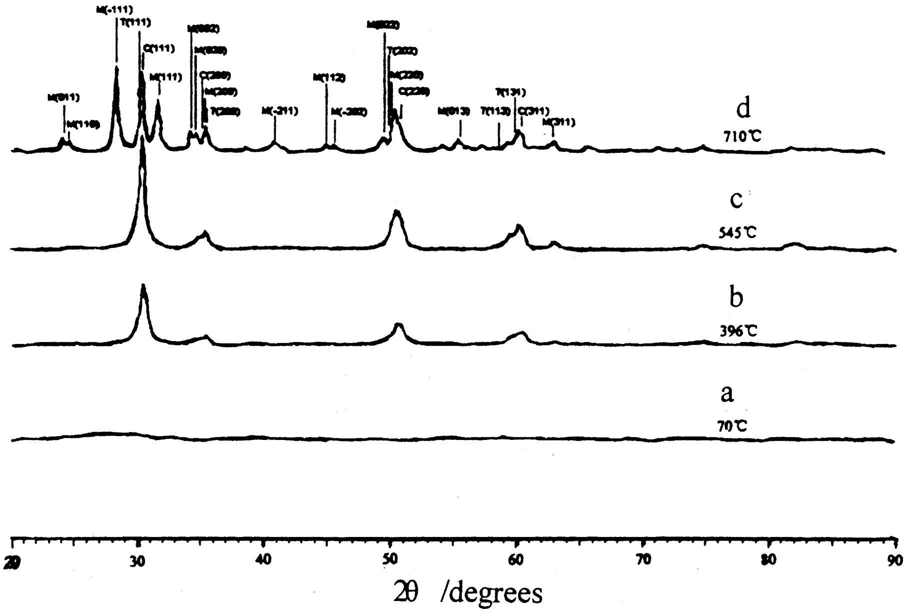

Fig. 4. XRD patterns of the zirconium acetate-complex (a) and its pyrolysis products at (b) 396, (c) 545, and (d) 710 °C.

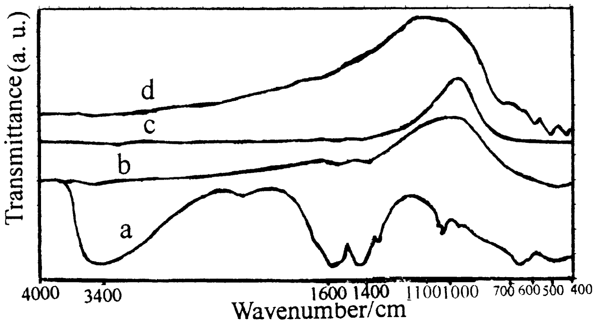

Fig. 5. IR spectra of the zirconium acetate-complex (a) and its pyrolysis products at (b) 396, (c) 545, and (d) 710 °C.

first exothermic peak may be ascribed to the decomposition of the major fraction of the precipitating complex, which gives rise to the formation of cubic and tetragonal zirconia. It is obvious that the crystallization of zirconia results from the pyrolytic breakdown of the acetate groups at ca. 396 °C with the evolution of acetone, carbon dioxide and water vapour.

Fig. 5c presents the infrared spectrum of the product derived from the heat treatment of the xerogel at 545 °C. It is clear that the bands belonging to the hydroxyl and the acetate groups almost disappear, indicating that the second exothermic peak is associated with the decomposition of the residual precipitating complex. In addition, elemental analyses show that only 1.23% of carbon and hydrogen-free remain in the product formed by the pyrolysis of the xerogel at 545 °C (Table 1), further confirming this assignment deduced by the infrared spectrum. Also, it should be pointed out that the phase transformation of zirconia occurs in the second exothermic step because the diffractogram (Fig. 4c) of the product derived from the second exothermic step displays diffraction peaks corresponding to the partial transformation of cubic to monoclinic and tetragonal zirconia, in other words, the diffractogram may be clearly indexed as a mixture consisting of a small amout (7%) of monoclinic zirconia as well as the prevalent cubic (52%) and tetragonal (41%) zirconia.

Finally, the XRD pattern (Fig. 4d) of the pyrolysis product at 710 °C shows a dominant presence of the monoclinic phase (61%) as well as a small amount of the cubic (27%) and tetrogonal (12%) phases. Consistent with the XRD result, the infrared spectrum (Fig. 5d) of the pyrolysis product at 710 °C exhibits the band at 735 cm^{-1} distinctive for the monoclinic phase, and the bands at 495, 415 and 575 cm^{-1} characteristic of the tetragonal, cubic and monoclinic phases, whereas the bands that represent the acetate group completely disappear. The infrared result is also supported by elemental analyses because they show that the pyrolysis product at 710 °C becomes essentially complete carbon-free (Table 1). Therefore, the temperature 710 °C provided by TGA is sufficient for calcining the xerogel to zirconia.

It can be realized from the above discussion that as the temperature for heat-processing the precipitating complex is increased in the order of 70, 396, 545 and 710 °C, the sequence of phase evolution is found to be amorphous→cubic and tetragonal→a small amount of monoclinic→slightly predominant monoclinic phase. Even for the high calcination temperature 710 °C, only a part of the cubic and tetragonal phases is transformed into the monoclinic phase. This is most likely related to the structure and concentration of the zirconium acetate-complex present in the solution, which are dependent on the pH value of the solution, because a strong pH dependency has been noticed in the formation, polymerization, and stoichiometry of some zirconium acetate complexes [5,6]. In Ref. [3], $Z_{r2}O(OH)\,(CH_3COO)_5\cdot 2H_2O$ was prepared by dissolving a small amount of zirconium oxychloride or carbonate in heavy excess of boiling pure acetic acid and then evaporating the resulting solution to a definite volume, suggesting that it was obtained under a strong acidic condition. In the present work, $Zr_4O_3(OH)_7\,(CH_3COO)_3\cdot 5H_2O$ was synthesized from zirconium oxychloride and acetic acid solution at pH ca. 6 and ambient temperature, resulting in the zirconium oxy-hydroxy-acetate containing more water molecules than that reported in Ref. [3] because in the present case (pH 6) hydroxyl ions would compete with acetate ions to form the acetate containing more hydroxyl and water. In addition, Table 2 shows that on calcinations at increasing temperature up to 710 °C, the increment of the crystallite size of the pyrolysis products is much pronounced and the relatively high monoclinic content will result. It is known that small crystallite size favourizes a tetragonal crystalline structure, and that

Table 1
Carbon and hydrogen contents in the xerogel and its pyrolysis products

Heat processing temperature (°C)	C (wt.%)	H (wt.%)
70	9.76	3.17
396	2.30	0.06
545	1.23	0.00
710	0.05	0.00

Table 2
Crystalline size and composition as a function of the temperature for heat-processing the xerogel

Heat processing (°C)	Crystallite size (nm)	Crystalline composition (%)		
		Monoclinic	Tetragonal	Cubic
396	24.3	0	34	66
545	30.4	7	41	52
710	113.1	61	12	27

the addition of aqueous ammonia provides hydroxyl ions in the amorphous material, which is conducive in stabilizing the tetragonal phase against conversion to the monoclinic polymorph.

The elemental analysis of the dried precipitating complex, i.e., xerogel, gave the following results (wt.%): Zr, 45.54; C, 9.76; H, 3.17; N and Cl, below the respective detection limit. The rest was referenced to oxygen (O, 41.53 wt.%). Based on the found values, the xerogel can be represented as a zirconium oxy-hydroxy-acetate: $Zr_4O_3\ (OH)_7\ (CH_3COO)_3{\cdot}5H_2O$, because the zirconium, carbon, hydrogen and oxygen contents calculated for the proposed acetate are 45.67, 9.01, 3.25, and 42.05, respectively, which agree well with the found values. On the other hand, according to the thermal gravimetric analysis as described above, the total loss of weight obtained after the thermal decomposition of the xerogel up to 710 °C is 38.52%, in other words, the zirconia content in the xerogel is 61.48%, namely, zirconium is equal to 45.54%, which is consistent with the found value from the elemental analysis and with the calculated one for the proposed acetate. In addition, the weight loss arisen from the dehydration of the xerogel is 10.95%, as found from TGA, is close to the calculated value (11.26%) for the coordinated water in the proposed acetate, $Zr_4O_3\ (OH)_7\ (CH_3COO)_3{\cdot}5H_2O$. In summary, the composition of the acetate proposed from the thermal gravimetric and elemental analyses shows that the xerogel studied is a basic zirconium acetate-complex, as judged by the infrared spectrum (Fig. 2). Because above pH 3 hydroxyl ions would compete with acetate ions, the resulting precipitate may be a hydroxy acetate complex. This study demonstrates that the zirconium oxy-hydroxy-acetate can yield a zirconia comparable to that formed from zirconium acetate solution by the other processes in the literature. Zirconia formed from zirconium acetate solution at 500 °C either by dessication and pyrolysis [4,5], by boiling under reflux [6] or by hydrolysis, drying and pyrolysis [7] exhibits crystalline size and composition similar to those of zirconia produced by the present process, as shown in Table 2. However, in the literature [1–3] the zirconium acetate or oxy-hydroxy-acetate was prepared by the reaction of zirconium chloride with excess of pure acetic acid below 80 °C under reduced pressure and then refluxing at the boiling point of the reactant, or by dissolving a small amount of zirconium oxychloride or carbonate in heavy excess of boiling pure acetic acid, evaporating the resulting solution to a definite volume, and then cooling and allowing it to stand for 12 h, whereas we synthesized a novel zirconium oxy-hydroxy acetate from zirconium oxychloride and acetic acid solution by a simple metalorganic precipitation process at a near-neutral pH and ambient temperature. In addition, only by calcining the zirconium oxy-hydroxy-acetate a comparable zirconia can be produced to that formed from zirconium acetate solution either by desiccation and pyrolysis [4,5], by boiling under reflux [6] or by hydrolysis, drying and pyrolysis [7]. In other words, the present route to a zirconium acetate and zirconia ceramics may eliminate the need for desiccating or boiling under reflux a precursor solution for a long period. It is, therefore, evident that the present process offers an easy access to a zirconium oxy-hydroxy-acetate and to zirconia ceramics from it with distinct advantages in terms of time-and energy-saving and environmental friendliness.

4. Conclusions

The present process can be considered as a competitive alternative to the existing synthetic routes to zirconium oxy-hydroxy-acetate, and offers distinct advantages in terms of time- and energy-saving and environmental friendliness. The exact and unequivocal assignments of the infrared bands for the zirconium oxy-hydroxy-acetate have supplemented the existing knowledge about the infrared spectra of zirconium acetates, and will be useful in disentangling the spectra of more complex molecules containing these groupings. In accordance with infrared spectral data, we are inclined to conclude that the precipitating complex is a basic zirconium acetate-complex in which an acetate ion is directly bonded to the zirconium of tetramer $[Zr_4\ (OH)_8]^{8+}$ mainly in a bridging bidentate coordination mode and the polymerization of the resulting tetramers can occur either through a COO^- group or through OH^- bridges. Also, the precipitating complex is identified as a new zirconium oxy-hydroxy-acetate $Zr_4O_3\ (OH)_7\ (CH_3COO)_3{\cdot}5H_2O$ by X-ray diffraction, differential thermal, thermogravimetric and elemental analyses, confirming the conclusion from the infrared study. Thermogravimetric and elemental analyses shows that the major fraction of the precipitating complex has been decomposed at 396 °C, resulting in a mixture of cubic and tetragonal zirconia, of which only a part will be transformed into monoclinic zirconia even at high calcination temperature 710 °C, as evidenced by X-ray diffraction study.

References

[1] R.C. Paul, O.B. Baidya, R.C. Kumar, R. Kapoor, Zirconium(IV) carboxylates, Aust. J. Chem. 29 (7) (1976) 1605–1607.

[2] N.W. Alcock, V.M. Tracy, T.C. Waddington, Acetates and acetate-complexes, Part 1. Preparation of acetate-complexes and conductimetric studies in the acetic anhydride solvent system. J. Chem. Soc. Dalton 21 (1976) 2238–2241.

[3] L.N. Kommisarova, New oxyacetates of zirconium and hafnium, Russ. J. Inorg. Chem. 8 (1) (1963) 56–62.

[4] M.L. Balmer, F.F. Lange, C.G. Levi, Metastable phase selection and partitioning in Z_rO_2–M_gO processed from liquid precursors, J. Am. Ceram. Soc. 75 (4) (1992) 946–952.

[5] A.C. Geiculescu, H.G. Spencer, Thermal decomposition and crystallization of aqueous sol–gel derived zirconium acetate gels:effects of the precursor solution pH, J. Sol-Gel Sci. Technol. 16 (3) (1999) 243–256.

[6] F.J. Berry, S.J. Skinner, I.M. Bell, R.J.H. Clark, C.B. Ponton, The influence of pH on zirconia formed from zirconium (IV) acetate solution: characterization by X-ray powder diffraction and Raman spectroscopy, J. Solid State Chem. 145 (2) (1999) 394–400.

[7] A. Samdi, B. Durand, M. Roubin, A. Daoudi, Pressing and sintering behaviour of yttria stabilized zirconia powders prepared from acetate solutions, J. Eur. Ceram. Soc. 12 (5) (1993) 353–360.

[8] G.Y. Guo, Z.F. Ni, Y.L. Chen, Crystallizability and sinterability of a precursor prepared by oxalate method in ethanol solution, J. Mater. Sci. 26 (13) (1991) 3511–3516.

[9] G.Y. Guo, Y.L. Chen, Effect of preparation methods and condition of precursors on the phase composition of yttria-stabilized zirconia powders, J. Am. Ceram. Soc. 75 (5) (1992) 1294–1296.

[10] N.B. Colthup, L.H. Daly, S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, 3rd edition, Academic Press Inc, New York, 1990.

[11] R.M. Silverstein, G.C. Bassler, T.C. Morrill, Spectrometric Identification of Organic Compounds, 5th edition, John Wiley & Sons Inc, New York, 1991.

[12] B.C. Smith, Infrared Spectral Interpretation, CRC Press, Roca Raton, 1998.

[13] L. Turi, J.J. Dannenberg, Melecular orbital study of acetic acid aggregation, 1. monomers and dimmers, J. Phys. Chem. 97 (47) (1993) 12197–12204.

[14] A. Burneau, F. Génin, F. Quilès, Ab initio study of the vibrational properties of acetic acid monomers and dimers, PCCP 2 (22) (2000) 5020–5029.

[15] F. Génin, F. Quilès, A. Burneau, Infrared and Raman spectroscopic study of carboxylic acids in heavy water, PCCP 3 (6) (2001) 932–942.

[16] G.B. Deacon, R.J. Pihllips, Relationships between the carbon–oxygen stretching frequencies of carboxylato complexes and the type of carboxylate coordination, Coord. Chem. Rev. 33 (1980) 227–250.

[17] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B, 5th edition, John Wiley & Sons Inc, New York, 1997.

[18] C.G. Barraclough, J. Lewis, R.S. Nyholm, Stretching frequencies of metal–oxygen double bonds, J. Chem. Soc. (11) (1959) 3552–3555.

[19] A.C. Geiculescu, H.G. Spencer, Thermal decomposition and crystallization of aqueous sol–gel derived zirconium acetate gels: effects of the additive anions, J. Sol–Gel Sci. Tech. 17 (1) (2000) 25–35.

[20] L.N. Komissarova, Z.N. Prozorovskaya, V.I. Spitsyn, Oxyacetates of zirconium and hafnium, Russ. J. Inorg. Chem. 11 (9) (1966) 2035–2040.

[21] B.P. Straughan, W. Moore, R. Mclaughlin, Structural investigations of zirconium tetra-acetate and the group IVB tetra-acetates, Spectrochim. Acta A42 (4) (1986) 451–456.

[22] S. Jana, P.K. Biswas, Chemical behaviour of zirconium oxychloride octahydrate and acetic acid in precursor solution for zirconia film formation on glass, J. Sol–Gel Sci. Technol. 9 (3) (1997) 227–237.

[23] F. Albert Cotton, Advanced Inorganic Chemistry, 3rd edition, John Wiley & Sons Inc, New York, 1972.

[24] W.A. Howard, T.M. Trnka, M. Waters, G. Parkin, Terminal chalcogenido complexes of zirconium: syntheses and reactivity of C_p2^*Zr (E) (NC_5H_5) (E = O, S, Se, Te), J. Organomet. Chem. 528 (1997) 95–121.

[25] G. Parkin, in: K. D. Karlin (ed.), Progress in Inorganic Chemistry, John Wiley & Sons Inc., New York, 1998, pp. 1–166.

[26] L. Prozorovskaya, N. Komissarova, V.I. Spitsyn, Oxypropionates of zirconium and hafnium, Russ. J. Inorg. Chem. 12 (10) (1967) 2553–2556.

[27] D.A. Powers, H.B. Gray, Characterization of the thermal dehydration of zirconium oxide halide octahydrates, Inorg. Chem. 12 (11) (1973) 2721–2726.

[28] D.W. Liu, C.H. Perry, R.P. Ingel, Infrared spectra in nonstoichiometric yttria-stabilized zirconia mixed crystals at elevated temperatures, J. Appl. Phys. 64 (3) (1988) 1413–1418.

[29] M. Kaklhana, M. Kotaka, M. Okamoto, Vibrational analysis of acetate ion molecules and estimation of equilibrium constants for their hydrogen isotopic exchange reactions, J. Phys. Chem. 87 (14) (1983) 2526–2535.

[30] E.V. Brusau, G.E. Narda, J.C. Pedregosa, Vibrational and thermal evidence of coordinated water and carboxylate groups in crystalline calcium malonate dihydrate, J. Solid State Chem. 143 (2) (1999) 174–181.