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Preparation of Polyzirconoxane from Zirconium Oxychloride Octahydrate and Ethylene Glycol as a Precursor for Zirconia Ceramics

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The preparation of polyzirconoxanes (EG-PZO) was investigated by a one-pot reaction of zirconium oxychloride octahydrate with ethylene glycol. Triethylamine was added dropwise into a mixture of zirconium oxychloride octahydrate, ethylene glycol and methanol to give EG-PZO with a good spinnability and stability to self-condensation. The ^{1}H NMR spectrum, IR spectrum, analytical data and expanded X-ray absorption fine-structure analysis indicated that EG-PZO consisted of Zr $<(OH)_2>$ Zr linkages as a main chain with pendant 2-hydroxyethoxy groups, chloro groups and water. The $3Y_2O_3$–$97ZrO_2$ ceramic fibers were prepared by sintering the precursor fibers after the addition of $Y(acac)_3$ (acac = acetoacetate) to EG-PZO.

Keywords: polyzirconoxane; zirconium oxychloride; ethylene glycol; one-pot reaction; EXAFS; zirconia; fibers; precursor

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INTRODUCTION

Zirconia (ZrO_2) is well known to be an excellent ceramic material with a high melting point, good mechanical properties at high temperatures and resistance to acid and alkali.[1–3] In particular, yttria-stabilized zirconia can be used both as an insulating material and for composite materials because of its high strength and toughness.[4,5] Zirconia ceramics or yttria-stabilized zirconia monoliths are often prepared by sintering zirconia powders. The production of zirconia fibers, thin films and coating films is best done using precursor methods. Here zirconia ceramics are obtained by sintering polyzirconoxanes that have been formed into desirable shapes.[6–9] In the preparation of zirconia ceramics by the precursor method, high ceramic yields and stability to gelation are essential, since modification by organic compounds not only increases the stability of precursor polymers and their ease in handling but also depresses the ceramic yield and the density of zirconia ceramics on sintering.

We have reported two routes to the synthesis of polyzirconoxanes which are stable to self-condensation, to prepare zirconia fibers (1) the acid-catalyzed hydrolytic polycondensation of zirconium chelates;[6,7] (2) the reaction of zirconium oxychloride with ethyl acetoacetate in the presence of triethylamine by a convenient one-pot synthesis.[8,9] The first route provides a stable polyzirconoxane with excellent ease of handling, which remains fluid for over one year, by a three-step reaction from zirconium tetrachloride via zirconium tetraisopropoxide and zirconium chelate. The second process gives an excellent processable form of polyzirconoxane via a one-pot reaction of zirconium oxychloride octahydrate with ethyl acetoacetate in the presence of triethylamine. In this work, we studied the preparation of polyzirconoxane (PZO) by a one-pot reaction of a novel zirconium oxychloride octahydrate (ZOC) with ethylene glycol; the product contains two fewer carbon atoms per polymer unit than that of ethyl

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$$ZrOCl_2 \cdot 8H_2O \xrightarrow[-Et_3NHCl]{EG,Et_3N/MeOH} \underset{EG-PZO}{[ZrCl(OCH_2CH_2OH)(OH)_2(H_2O)]_n} \quad [1]$$

$$EG-PZO \xrightarrow{Y(acac)_3} \xrightarrow{spinning} \xrightarrow{pyrolysis} 3Y_2O_3-97ZrO_2 fibers \quad [2]$$

acetoacetate, and the fabrication of zirconia fibers partially stabilized with yttria according to Eqns [1] and [2].

EXPERIMENTAL

One-pot synthesis of polyzirconoxane (No. 5) [EG-PZO (No. 5)]

Triethylamine (9.39 g) was added dropwise to a mixture of zirconium oxychloride octahydrate (ZOC, 24.67 g) and ethylene glycol (EG, 9.55 g) in methanol (300 ml) below 5 °C. After stirring for 2 h at room temperature, 1 M HCl (15.4 ml) was added dropwise to the reaction mixture, and then stirring was continued for 3 h at room temperature. The solvents were removed under reduced pressure to give white solids, and then chloroform was added to dissolve the triethylamine hydrochloride salt followed by filtration to isolate EG-PZO as a white powder.

Preparation of $3Y_2O_3$–$97ZrO_2$ fibers

EG-PZO (No. 5) powder and trisacetylacetonatoyttrium [Y(acac)$_3$] were dissolved in methanol in the ratio $Y_2O_3/ZrO_2 = 3:97$. Evaporation of the solvent gave a highly viscous and homogeneous yttrium-containing EG-PZO solution, which, at concentration of 63.3 and 64.5 wt%, was poured into a spinning nozzle and pressurized to 8.0 kgf cm^{-2} by nitrogen gas to extrude $3Zr_2O_3$–$97ZrO_2$ precursor fiber from a pinhole (0.15 mm i.d.).[9] The $3Zr_2O_3$–$97ZrO_2$ precursor fiber thus formed was wound on to a spinning drum at 30 m min^{-1}.

$3Y_2O_3$–$97ZrO_2$ fibers were obtained by drying the precursor fibers at 80 °C for 2 h, heating in air at 2 °C min^{-1} to the desired temperature, and pyrolyzing at the desired temperature for 1 h.

Instruments and analysis

^{1}H NMR spectra were measured using a JEOL PMX60SI spectrometer in [$^2H_4$]methanol.

The cross-polarization/ magic-angle spinning (CP/MAS) solid-state ^{13}C NMR spectrum was recorded using a JEOL JNM-EX400 spectrometer.

Infrared (IR) spectra were recorded with a Hitachi 260-50 IR spectrophotometer by the KBr disk method.

X-ray diffractograms were obtained by using a Rigaku Denki model CN-2013 instrument.

The zirconium content of EG-PZO was determined as follows. An EG-PZO/methanol solution (10 ml, 1.14×10^{-2} mol^{-1}) was boiled at 100 °C for 5 min with 61% nitric acid (11.23 ml) and deionized water (38.77 ml). The solution was titrated using aqueous ethylenediamine tetra-acetic acid (EDTA) in the presence of XO indicator.

The chlorine content of EG-PZO was determined by the Vorhard method. A 0.1 g sample of EG-PZO was weighed and then added to 10 ml of 0.1 M $AgNO_3$ aq. solution. The solution was titrated with aqueous NH_4SCN (0.025 M) in the presence of Halotrichite indicator and nitrobenzene (6 ml).

Zr K-edge EXAFS measurements were conducted *in situ* in transmission mode at BL-10B Photon Factory (Proposal no. 94G214) at the National Laboratory for High-Energy Physics (KEK-PF) with an Si(311) channel-cut monochromater. The spectra were measured at room temperature. A solid sample was measured as a pressed pellet with polyethylene glycol, and a liquid sample was measured in a vessel made from polyethylene. Equation [3] was used for the curve-fitting analysis of EXAFS data, where k is the photoelectron wave number, $f_i(k,\pi)$ is the back-scattering amplitude function, and $\delta_i(k)$ is the phase-shift function.

$$\chi_i(k) = N_i|f_i(k,\pi)| \exp(-2\sigma^2k^2) \sin(2kR_i + \delta_i(k))/kR_i^2 \quad [3]$$

For $f_i(k,\pi)$ and $\delta_i(k)$ either the theoretical or

empirical form was chosen, depending on the system. The model compound for Zr—O and Zr—Zr was ZOC, whose structure was determined by X-ray analysis[10] (Fig. 1). Theoretical parameters determined by McKale *et al.* were used for the analysis of the first shell.[11] These parameters are not recommended by the International XAFS Committee. However, we will discuss only the change in structure, and not the absolute structure. Moreover, we carefully checked the validity of these parameters using the reference compounds in Table 1. Comparing the results of the curve-fitting for ZOC dissolved in H_2O with the crystalline materials in Table 1, we conclude that good agreement was achieved with the empirical amplitude and phase functions exhibited by crystalline ZOC. In H_2O solution, the structure of ZOC consists of a cyclic tetrameric units derived from crystalline ZOC, as reported by Devia and Sykes.[12] Summarizing the EXAFS results of ZOC dissolved in H_2O, we conclude that the use of these parameters in the simulation of the EXAFS spectra is reasonable. The errors were estimated according to the *Report on Standards and Criteria in XAFS Spectroscopy*.[13]

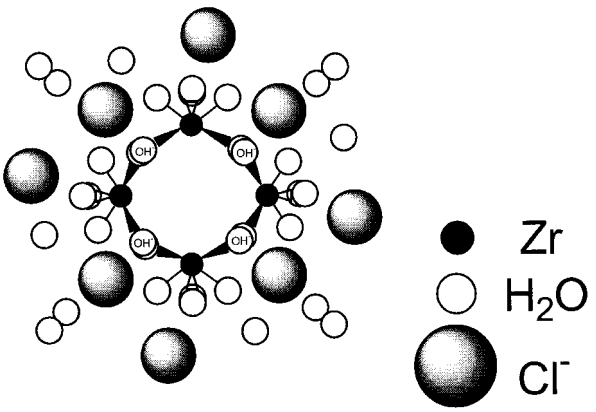

Figure 1 Crystal structure of ZOC.[10].

RESULTS AND DISCUSSION

Synthesis and properties of EG-PZO

EG-PZO was purified and isolated by extracting triethylamine hydrochloride with chloroform from the reaction mixture. After filtration of the chloroform solution, the residue was rinsed with chloroform and dried to give EG-PZO in almost quantitative yield. However, the properties of EG-PZO varied, based on the reaction conditions shown in Table 2. A white gel formed in Run 1 when triethylamine was used in a molar Et_3N/ZOC ratio of 2.0:1. The solubility of EG-PZO increased slightly with a decrease in triethylamine from 1.4 to 1.2:1. In Runs 4 and 5, a slightly yellow powder, soluble in methanol, formed. The methanol solution of EG-PZO allowed fibers of 50–1cm to be drawn for Runs 4 and 5, respectively. The elemental analysis of these samples revealed that the chlorine was removed quantitatively by adding triethylamine.

Triethylamine promotes the reaction by removing its hydrogen chloride salt. The elemental analysis of EG-PZO (No. 3) indicates the quantitative removal of hydrogen chloride. A stable and

Table 1 Curve-fitting analytical data in the EXAFS analysis of ZOC and EG-PZO (No. 5)[a]

Sample	Shell	r (Å)	N	σ (Å)
ZOC[b]	O	2.24	8.0	0.06
	Zr	3.57 ± 0.01[c]	2.0	0.06
ZOC in H_2O	O	2.25 ± 0.01	8.2 ± 0.7	0.052 ± 0.008
	Zr	3.60 ± 0.01	2.2 ± 0.3	0.072 ± 0.004
EG-PZO (No. 5)	O	2.24 ± 0.02	7.4 ± 1.0	0.041 ± 0.021
	Cl	3.31 ± 0.04	1.0 ± 0.4	0.070 ± 0.026
	Zr	3.57 ± 0.02	1.4 ± 1.0	0.077 ± 0.014
EG-PZO (No. 5) in MeOH	O	2.25 ± 0.02	7.9 ± 1.5	0.059 ± 0.021
	Cl	3.28 ± 0.04	0.6 ± 1.2	0.049 ± 0.058
	Zr	3.56 ± 0.02	2.1 ± 0.8	0.091 ± 0.012

[a] r = distance; N = coordination number σ = Debye–Waller factor.
[b] Ref. 10.
[c] Determined on the bases of the theoretical parameters in Ref. 11.

Table 2 Preparation conditions, properties, yield and analysis of EG-PZO[a]

No	Molar ratio		Spinnability (cm)	Yield (g)	Elemental analysis (%)		
	Et_3N/ZOC	HCl/ZOC[b]			Zr	Cl	Cl/Zr[c]
1[d]	2.0	—	—	—	—	—	—
2[d]	1.4	—	—	—	—	—	—
3[d]	1.2	—	—	17.9	38.8	12.2	0.81
4[e]	1.0	—	50	17.7	38.1	14.3	0.96
5[e]	1.2	0.2	>100	18.1	38.1	14.3	0.97

[a] Reaction conditions: at room temperature for 2 h. ZOC in operation was 24.67 g (0.077 mol). Solvent: methanol (300 ml).
[b] HCl aq. was added after the filtration of Et_3NHCl.
[c] Molar ratio.
[d] EG-PZO (Nos 1, 2 and 3) were insoluble in common organic solvents.
[e] EG-PZO (Nos 4 and 5) were soluble in methanol and insoluble in other common organic solvents.

soluble EG-PZO (Nos 4 and 5) was obtained when the molar ratio of Cl/Zr was almost 1:1, regardless of the procedures. The addition of triethylamine in the molar ratio $EG/Et_3N = 1:1$ and especially 1:1.2 followed by the addition of hydrogen chloride in the molar ratio ZOC/HCl = 1:0.2. Livage et al, reported that the reaction of zirconium tetraisopropoxide with ethylene glycol[14] led to network formation, in which two zirconium atoms combined with one ethylene glycol molecule. Network formation, however, would be obstructed by the chloride anion for EG-PZO (Runs 4 and 5).

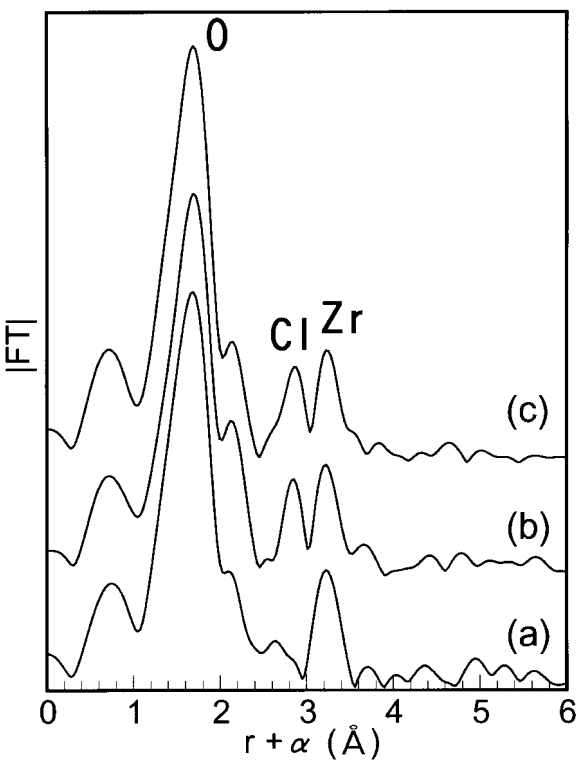

Figure 2 Fourier transforms of k^3-weighted EXAFS spectra of (a) ZOC dissolved in MeOH; (b) EG-PZO (No. 5) dissolved in MeOH; (c) EG-PZO (No. 5) powder.

The IR spectrum of EG-PZO (No. 5) exhibits absorption peaks at 3400 (ν_{OH}), 2940 (ν_{CH}), 1350 (ν_{CH_2}), 1450 (ν_{CH_2}) 1080 (ν_{CO}) and 450 cm^{-1} (ν_{ZrO}). The ^1H NMR spectrum of EG-PZO (No. 5) indicates methylene (—CH_2—), hydroxy and methoxy groups at 4.10, 4.91 and 3.32 ppm, respectively. The CP/MAS solid-state ^{13}C NMR spectrum showed a broad signal around 67.0 ppm, which is ascribed to the methylene (—CH_2—) group. The coordination of ethylene glycol was estimated from the chemical shift of the methylene group: The signals appear around 31.2 and 70.6 ppm when the ethylene glycol acts as an intramolecular chelating agent and an intermolecular bridging agent, respectively.[14] The ethylene glycol in EG-PZO (Run 5) is suggested to act as an intermolecular bridging agent.

The EXAFS spectra of ZOC and EG-PZO (No. 5) were recorded and interpreted in the same way as the data for ZOC dissolved in H_2O. Figure 2 shows the EXAFS functions $k^3\chi(k)$ and the corresponding Fourier-transformed functions. The Fourier-transformed functions of ZOC and EG-PZO (No. 5) are very similar except for the appearance of a Zr–Cl shell in EG-PZO (No. 5). This spectral change suggests the conformational change of chlorine by the addition of triethylamine.

The theoretical simulation of the EXAFS spectrum was started using the parameter values of ZOC for the Zr–O and Zr–Zr shells and the theoretical parameter for the Zr–Cl shell. The curve-fitting

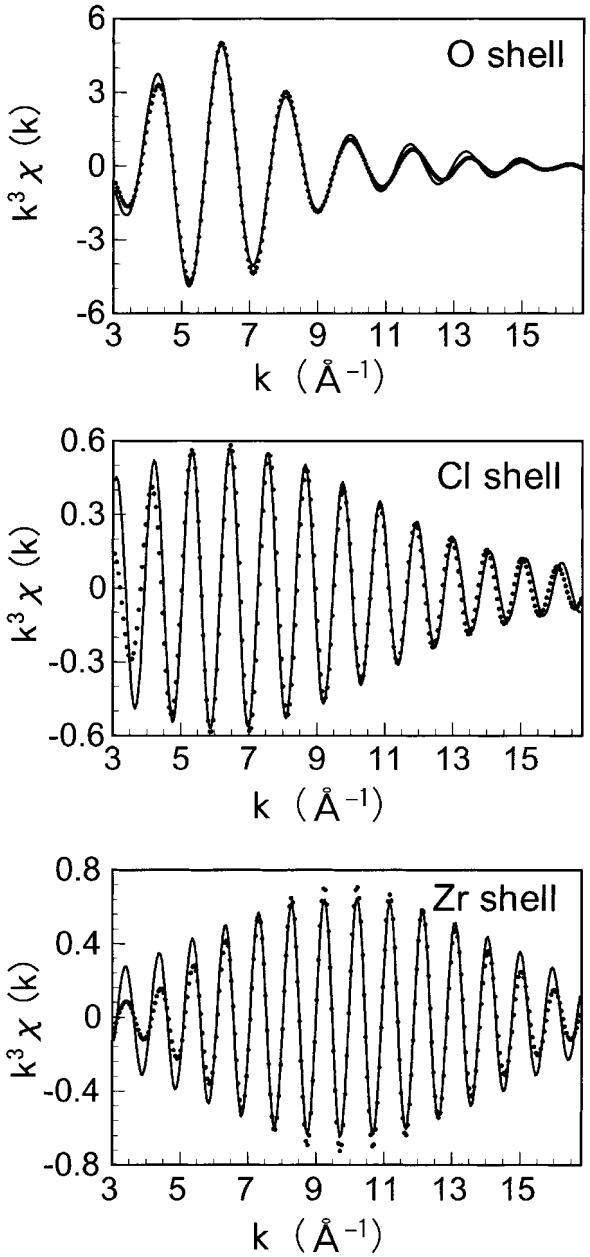

Figure 3 Least-squares curve fits (dotted lines) and the Fourier-fitted k^3-weighted EXAFS spectra (solid lines) for EG-PZO (No. 5) powder.

results are shown in Fig. 3 together with the distance and coordination numbers obtained as shown in Table 1. The bond length and coordination number of Zr–O for EG-PZO (No. 5) were in good agreement with those of ZOC, which indicates that the state of Zr–O shells in EG-PZO (No. 5) was very similar to that of ZOC. In Zr–Zr shells, the bond length of EG-PZO (No. 5) agrees with that of ZOC, with some variation in the coordination numbers: 2.8 ± 1.0 for ZOC in methanol and 2.1 ± 0.8 for EG-PZO (No. 5) in methanol. These results indicate that the ZOC forms a cluster in methanol based on the tetrameric units, and the EG-PZO (No. 5) is a trimer or tetramer. On the other hand, the Zr–Cl bond length for EG-PZO was 3.28 ± 0.04 Å, which is greater than the sum of the ionic radii of Zr and Cl, 2.52 Å. The chlorine atom may be ionically bonded to zirconium.

Since EG-PZO (No. 5) is only soluble in methanol, its molecular weight was not analyzed. The analytical and calculated values summarized in Table 3 are in good agreement with those of the estimated structures. In addition, the OH/CH_2 proton ratio in the NMR spectrum is estimated to be 1.25:1, corresponding to five or six hydroxy protons to one 2-hydroxyethoxy group.

A plausible EG-PZO unit structure (No. 5) is shown in Fig. 4. A zirconium atom is attached to four hydroxy groups, one 2-hydroxyethoxy group, one water and one chlorine atom. The hydroxy in the 2-hydroxyethoxy group coordinates to another neighboring zirconium atom by hydrogen bonding, which is shown by bold and italic characters in Fig. 4. The structure of EG-PZO is considered to be fundamentally based on the structure of ZOC with a slight modulation such as replacement of water and a chlorine atom with a 2-hydroxyethoxy group. The coordination numbers of oxygen, zirconium and chlorine atoms for a zirconium atom, the proton ratio of OH/CH_2 and the elemental analysis showed fairly good agreement between the observed values and the calculated values based on the structure shown in Fig. 4.

Preparation of $3Y_2O_3$–$97ZrO_2$ fibers

Y-EG-PZO (No. 5) was prepared as a viscous methanolic solution of EG-PZO (No. 5) with trisacetylacetonatoyttrium in the molar ratio of $Y_2O_3/ZrO = 3:97$. Y-EG-PZO (No. 5) provided precursor fibers by mechanical dry spinning of the solution. On pyrolysis, the white precursor fibers became black (400 °C), gray (600 °C) and then white (800 °C). Figure 5 (a) shows an SEM image of the precursor fiber with an ellipsoidal cross-section and a diameter of 50–70 μm. On the other hand, as shown in Fig. 5 (b), after pyrolysis at 1000 °C the fiber shrunk with many cracks, which result from degradation of organic groups in the

Table 3 Analytical and calculated data for EG-PZO

	Analysis for EG-PZO (No. 6)	Calculated for the structure in Fig. 4
Average of the neighboring atoms: O	7.4 ± 1.0	7.0
Cl	1.0 ± 0.4	1.0
Zr	1.4 ± 1.0	2.0
^{1}H NMR proton ratio of OH/CH_2	1.35	1.25
Elemental analysis (%): Zr	38.1	38.0
Cl	14.3	14.8
Molar ratio of Cl/Zr	0.97	1.0

precursor fibers. The $3Y_2O_3$–$97ZrO_2$ ceramic fibers were brittle and they broke into pieces after pyrolysis at 1000 °C.

The IR spectra of $3Y_2O_3$–$97ZrO_2$ fibers on heating (Fig. 6) indicated the decrease in organic groups up to 300 °C and the decrease in hydroxy groups up to 800 °C. The absorption peak due to Zr–Cl linkage was not observed clearly in all IR spectra. The IR spectral change indicates the oxidative degradation of the organic groups up to 300 °C. The X-ray diffractograms (Fig. 7) showed the diffraction pattern ascribed to the crystallization of zirconia at $\geq$400 °C, which supports the formation of tetragonal zirconia. The increase of the peak intensity with a narrow peak width supports the increase in crystallite size of tetragonal zirconia on pyrolysis. Moreover, the absence of monoclinic and cubic zirconia strongly supports the formation of zirconia fibers partially stabilized with yttria.

These observations and spectral behavior support the transformation of Y-EG-PZO (No. 5) to zirconia fibers: when precursor fibers made from Y-EG-PZO (No. 5) were pyrolyzed, the organic groups and chlorine were eliminated to provide zirconia fibers.

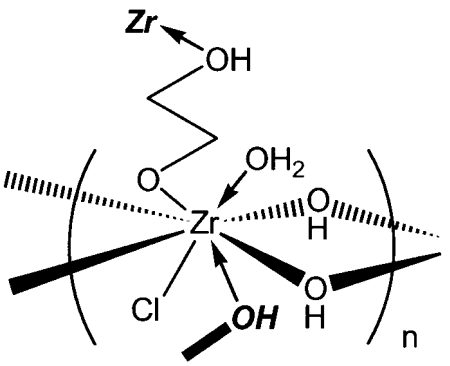

Figure 4 A possible structure of EG-PZO.

Zirconia fibers partially stabilized with yttria were reported in our previous papers, in which we described how the precursor fibers were steam-hydrolyzed to eliminate organic moieties to form porous fibers. The porous fibers were then sintered to afford ceramic fibers, which crystallized in the tetragonal phase with a tensile strength of 1.5 GPa.[9] On the other hand, the zirconia fibers partially stabilized with yttria prepared from Y-EG-PZO

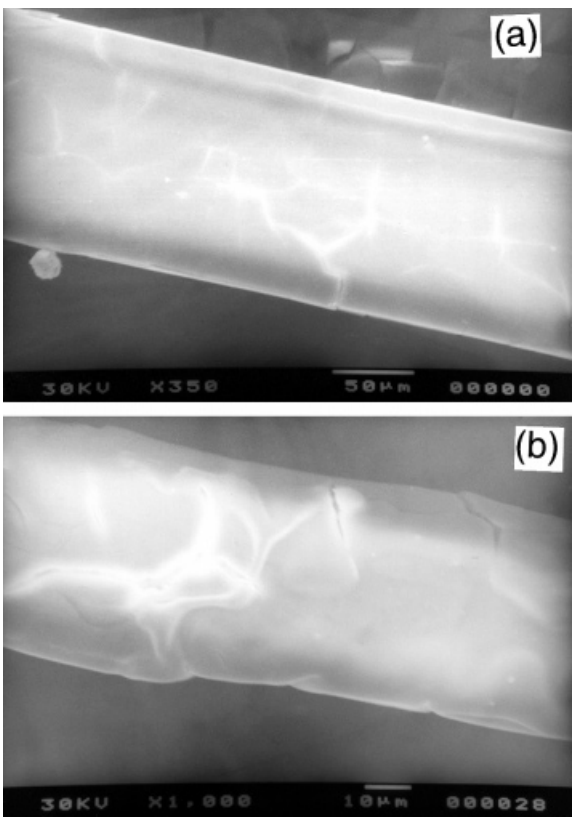

Figure 5 SEM image of the $3Y_2O_3$–$97ZrO_2$ fibers (a) before and (b) after pyrolysis at 1000 °C for 1 h.

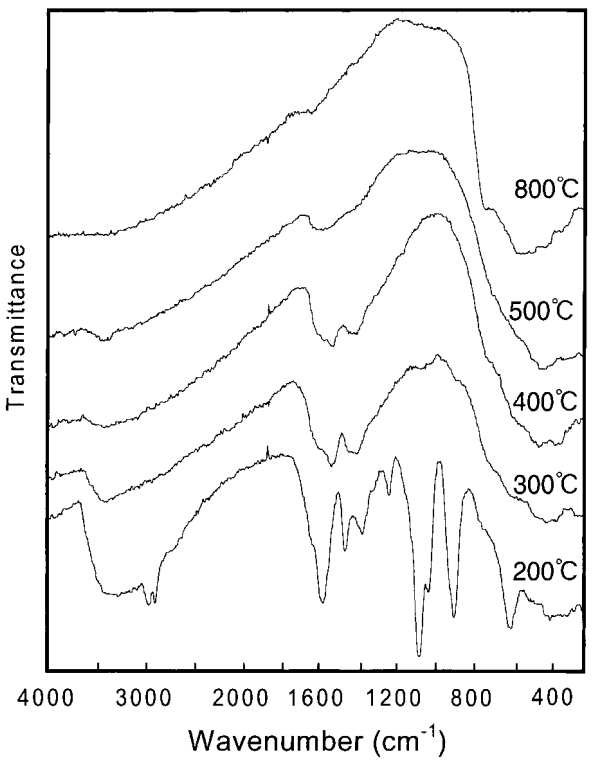

Figure 6 IR spectra of $3Y_2O_3$–$97ZrO_2$ fibers pyrolyzed at various temperatures (KBr disk method).

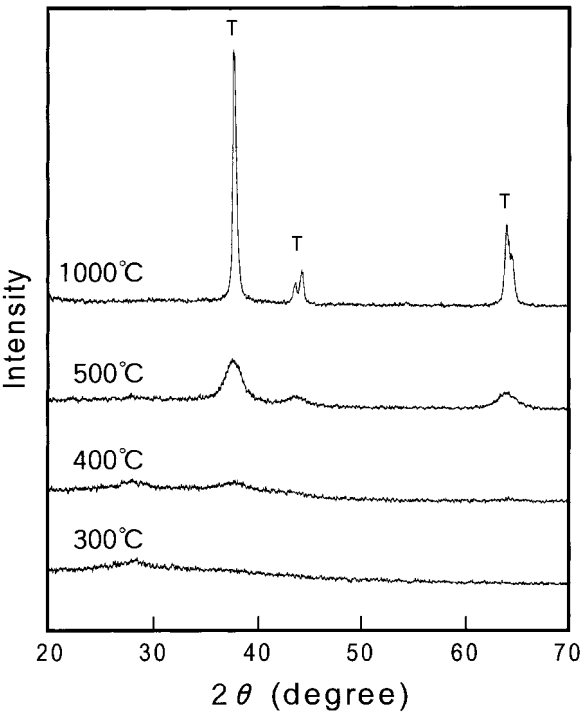

Figure 7 XRD patterns of zirconia partially stabilized with yttria, prepared by sintering $3Y_2O_3$–$97ZrO_2$ fibers at various temperatures (T, tetragonal, $Fe_{K\alpha}$).

(No. 5) were brittle, with many cracks. Since Y-EG-PZO (No. 5) was found to be soluble in hot water, we could not stem-treat precursor fibers. The remaining organic moieties and chlorine may produce a large strain upon elimination, which results in the formation of brittle ceramic fibers with many cracks.

CONCLUSIONS

Polyzirconoxane (EG-PZO) with good spinnability and stability against gelation was prepared by the one-pot reaction of zirconium oxychloride octahydrate with ethylene glycol in the presence of triethylamine. EG-PZO was stable to gelation when the zirconium/chlorine molar ratio of was 1:1. The elemental analysis, NMR, IR and EXAFS spectra showed that EG-PZO consisted of Zr $<(OH)_2>$ Zr linkages with pendant 2-hydroxyethoxy groups, chloro groups and water.

The dry-spinning of $Y(acac)_3$ added EG-PZO provided precursor $3Y_2O_3$–ZrO_2 fibers. The pyrolysis of the precursor fibers provided $3Y_2O_3$–ZrO_2 ceramic fibers with the elimination of chlorine and combustion of carbon.

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REFERENCES

1. N. Yamamoto, *Ceram. Sci. Technol. Present and Future* **18**, 375 (1981).
2. H. Abe, *Eng. Ceram.* **23**, 1 (1984).
3. S. Hori, *Kyojin Zirconia*, Uchida Rohkaku Ho, 1990, p. 139.
4. K. Kobayashi, K. Shinjo and T. Masaki, *Ceram. Sci. Technol. Present and Future* **10**, 401 (1981).
5. R. C. Garvie, R. H. Hannink and R. T. Pascoe, *Nature (London)* **258**, (557), 703 (1975).
6. Y. Abe, Y. Kimata, T. Gunji, Y. Nagao and T. Misono, *Seramikkusu Ronbunshi* **97**, 596 (1989).
7. T. Gunji, H. Goto, Y. Kimata, Y. Nagao, T. Misono and Y.

Abe, *J. Polym. Sci. Part A: Polym. Chem. Ed.* **30**, 2295 (1992).
8. Y. Abe, H. Tomioka, T. Gunji, Y. Nagao and T. Misono, *J. Mater. Sci. Lett.* **13**, 960 (1994).
9. Y. Abe, T. Kudo, H. Tomioka, T. Gunji, Y. Nagao and T. Misono, *J. Mater. Sci.* **33**, 1863 (1998).
10. A. Clearfield and P. A. Vaughan, *Acta Crystallogr* **9**, 555 (1955).
11. A. D. McKale, B. W. Veal, A. P. Pailikas, C. K. Chan and G. S. Knapp, *J. Am. Chem. Soc.* **110**, 3764 (1988).
12. D. H. Devia and A. G. Sykes, *Inorg. Chem.* **20**, 910 (1981).
13. F. W. Lytle, D. E. Sayers and E. A. Sterm, *Physica B (Amsterdam)* **158**, 701 (1989).
14. J. Chaibi, M. Henry, H. Zarrouk, N. Gharbi and J. Livage, *J. Non-Crystal. Solids* **170**, 1 (1994).

