JOURNAL OF MATERIALS SCIENCE 25 (1990) 3922–3929

Preparation of multiple oxide $BaTiO_3$ fibres by the sol–gel method

TOSHINOBU YOKO*, KANICHI KAMIYA, KATSUHISA TANAKA†
Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie-ken 514, Japan

Multiple oxide $BaTiO_3$ gel fibres were prepared by the sol–gel method from $Ba(OC_2H_5)_2$–$Ti(O\text{–}isoC_3H_7)_4$–H_2O–C_2H_5OH–CH_3COOH and $Ba(CH_3COO)_2$–$Ti(O\text{–}isoC_3H_7)_4$–H_2O–CH_3COOH solutions. Relatively long gel fibres of 10 cm length were obtained from both solutions in the limited composition region. The latter solution in particular showed a spinnability even when it contained no water. Therefore, the occurrence of spinnability of the solution was considered to be due to the formation of linear polymers composed of bridging acetate groups such as $Ti \leftarrow O\text{–}C(CH_3)\text{–}O\text{–}Ti$ rather than metalloxane bonding as Ti–O–Ti. Addition of water to the solutions seems to break the bridging acetate bonds and replace some of them by bridging oxygen bonds. The as-drawn gel fibres which were X-ray amorphous crystallized into $BaTiO_3$ ceramic fibres of 5 mm average length upon heating above 600° C. However, the gel fibres drawn from the sols without water became powdery on heating because of the lack of Ti–O–Ti metalloxane bonds. The crystallization behaviour of the $BaTiO_3$ gel fibres is discussed based on the infrared spectroscopy, X-ray diffraction analysis and thermogravimetric–differential thermal analysis.

1. Introduction

Preparation of ultrafine oxide powders by hydrolysis of metal alkoxides is now one of the most important techniques to obtain raw materials from which dense ceramic bodies are fabricated [12]. This method is considered to be very powerful especially for preparing multiple oxide ceramics, because both fineness and homogeneity of powders can be attained at the same time as long as the corresponding metal alkoxides are intimately mixed in a liquid state and then subjected to hydrolysis and condensation [1–3].

Metal alkoxides are also excellent precursors for making ceramic fibres through hydrolysis and condensation [4]. We recently reported the preparation of relatively long ceramic fibres of TiO_2 [5], and ZrO_2 and $CaO\text{–}ZrO_2$ [6, 7] by heating the gel fibres drawn from the sol which were obtained simply by hyrolysing the corresponding metal alkoxides under very carefully controlled conditions without adding a viscosity increasing agent. There are potential demands for ceramic fibres to be used for reinforcing ceramic and metal bodies. Moreover, very recently the superconducting $BaY_2Cu_3O_{7-x}$ fibres have been prepared by the sol–gel method using the corresponding metal acetates as the starting materials [8, 9].

In the present study, an attempt to prepare ceramic fibres of multiple oxide $BaTiO_3$, which is one of the most important ferroelectric materials, has been made utilizing the sol–gel method. The mechanisms of the formation of $BaTiO_3$ linear polymers in the sol and the conversion of the drawn fibrous precursor gels into ceramic fibres have been investigated using infrared spectroscopy, X-ray diffraction and thermogravimetric–differential thermal analysis (TG–DTA) measurements.

2. Experimental procedure

2.1. Preparation of $BaTiO_3$ sol

$BaTiO_3$ sols were prepared with and without ethanol. In both cases, glacial acetic acid was used as a catalyst instead of HCl, because Cl^- ions would react with Ba^{2+} ions to form an undesirable $BaCl_2$ which does not decompose on heating to higher temperatures.

2.1.1. Use of anhydrous ethanol as a solvent

In the first method, barium metal, whose surface was polished with emery paper in kerosene, was allowed to react with anhydrous ethanol in a nitrogen atmosphere at room temperature to form $Ba(OC_2H_5)_2$. Then an ethanolic solution of $Ti(O\text{–}isoC_3H_7)_4$ was added slowly to the $Ba(OC_2H_5)_2$ ethanol solution with a syringe to yield a yellow muddy solution, which, in turn, was peptized by glacial acetic acid. The total amounts of added C_2H_5OH ranged from 2 to 18 in molar ratio to the total alkoxides. The amount of acetic acid required to produce a clear sol depended on the composition of the starting solutions. After stirring vigorously, the prescribed amount of water was added dropwise using a burette. The whole process is schematically depicted in Fig. 1 (broken line).

---

* *Present address*: Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto-fu 611, Japan.

† *Present address*: Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan.

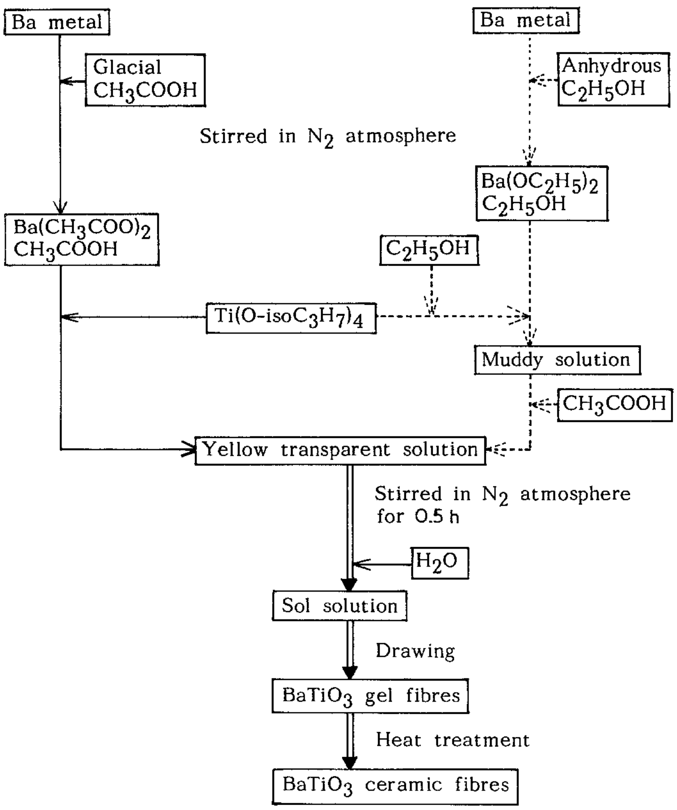


Figure 1 Flow chart of preparation of BaTiO$_3$ fibres using (- - -) ethanol and (——) glacial acetic acid as a solvent.

2.1.2. Use of glacial acetic acid as a solvent

In the second case, barium metal was allowed to react directly with excess glacial acetic acid instead of anhydrous ethanol, in a nitrogen atmosphere at room temperature to form Ba(CH$_3$COO)$_2$. Ti(O-isoC$_3$H$_7$)$_4$ was added slowly to the solution with a syringe. Then the mixture was stirred vigorously for 30 min. The resultant solution was transparent and yellow in colour. The prescribed amount of water was also added to the solution. The flow chart of this process is schematically shown in Fig. 1 (solid line).

2.2. Ageing of the sol

The sols thus prepared were subjected to ageing at 30, 60 and 80° C. Gelation time, however, was too short for gel fibres to be drawn from the sol when reaction temperatures of 60 and 80° C were adopted. Therefore, subsequent ageing was carried out exclusively at 30° C.

2.3. Fibre drawing

Spinnability of the sol was checked simply by dipping a glass rod of 6 mm diameter in the sol and then pulling it up. From the sols which were spinnable, gel fibres were drawn continuously by a rotary spinning device in an ambient atmosphere where relative humidity was kept at 70%.

2.4. Heat treatment of BaTiO$_3$ gel fibres

In order to convert fibrous gels into ceramic fibres, the drawn BaTiO$_3$ gel fibres were heated to temperatures from 100 to 1300° C at 100° C intervals for 1 h. Then a heating rate of 2° C min^{-1} was adopted. Identification of the precipitated crystals was made using a powder X-ray diffraction technique. The crystallite size was determined from the full-width at half-maximum (fwhm) using Scherrer's equation [10].

The crystallization behaviour was also monitored using a TG-DTA machine (model TG-DTA 8112BH, Rigaku, Japan). The Curie point of the BaTiO$_3$ fibres which were heat treated at temperatures from 800 to 1300° C at 100° C intervals was also determined from DTA measurement.

In addition, infrared spectroscopy was used to trace the thermal evolution of the structure of BaTiO$_3$ gel fibres.

3. Results

3.1. Spinnability-composition relation

Fig. 2a shows a spinnability-composition relation in the system Ba(OC$_2$H$_5$)$_2$-Ti(O-isoC$_3$H$_7$)$_4$-H$_2$O-C$_2$H$_5$OH-CH$_3$COOH. The added amounts of acetic acid were not constant, but varied from 5 to 6.3 in molar ratio to the alkoxides, depending on the composition of the solution.

The spinnability was observed in the composition region from 3 to 6 and from 0.5 to 4 in molar ratios of C$_2$H$_5$OH and H$_2$O to [Ba + Ti(O-isoC$_3$H$_7$)$_4$, respectively. the asterisk in the figure indicates that barium metal remained unreacted due to the presence of very little alcohol. However, continuous gel fibres could not be drawn from these sols with the rotary spinning device, probably because of the dilution effect of ethanol, although fibres could be barely drawn by hand.

Fig. 2b shows a spinnability-composition relation in the system Ba(CH$_3$COO)$_2$-Ti(O-isoC$_3$H$_7$)$_4$-H$_2$O-CH$_3$COOH containing no ethanol. The spinnable region (○) was observed in the composition region from 4 to 6 and from 0 to 1 in molar ratios of CH$_3$COOH and H$_2$O to [Ba + Ti(O-isoC$_3$H$_7$)$_4$], respectively. In particular, from the solution with the composition of 4 and less than unity in the molar ratios of CH$_3$COOH and H$_2$O to [Ba + Ti(O-

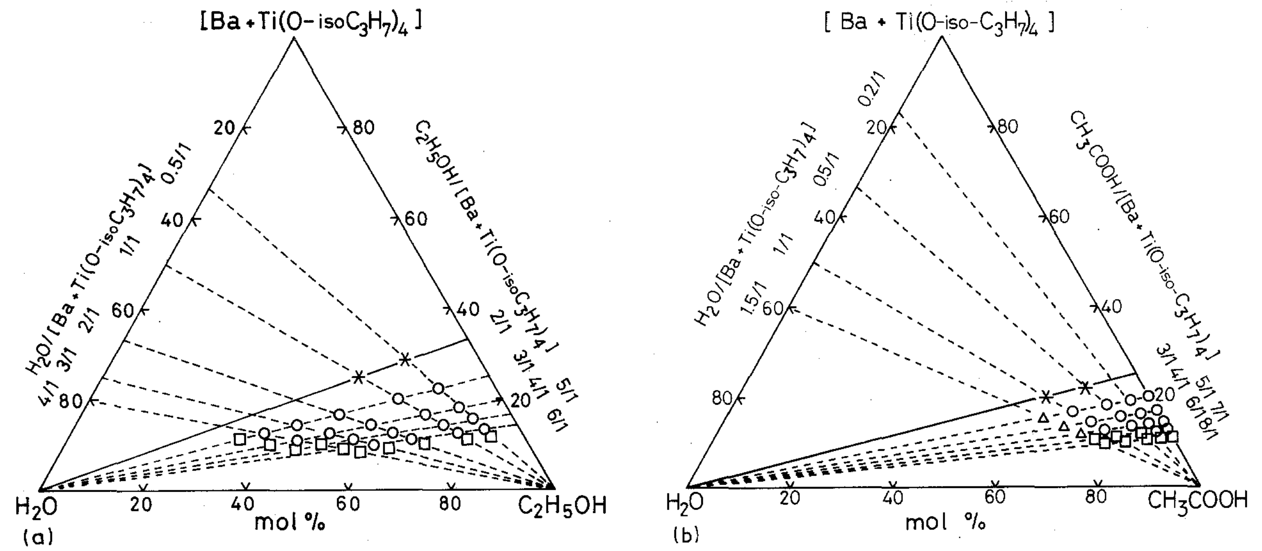


Figure 2 Spinnability–composition in the systems (a) Ba(OC$_2$H$_5$)$_2$–Ti(O–isoC$_3$H$_7$)$_4$–H$_2$O–C$_2$H$_5$OH–CH$_3$COOH and (b) Ba(CH$_3$COO)$_2$–Ti(O–isoC$_3$H$_7$)$_4$–H$_2$O–CH$_3$COOH. (*) Immisible, (○) spinnable, (□) not spinnable, (△) precipitation.

isoC$_3$H$_7$)$_4$], respectively, relatively long gel fibres of ~ 10 cm in length were obtained. In this case, continuous gel fibres could be successfully drawn with the rotary spinning device. Therefore, in subsequent experiments the gel fibres were drawn from the sol without ethanol. Both open squares and triangles in the figure show that the solutions were unspinnable, where triangles mean that precipitation took place during addition of water.

3.2. Appearance of gel fibres

The pictures of BaTiO$_3$ gel fibres drawn from the sols with compositions of [Ba + Ti(O–isoC$_3$H$_7$)$_4$] : H$_2$O : CH$_3$COOH = 1 : 0.5 : 4 and = 1 : 0 : 4 are shown in Figs 3a and b, respectively. Although as-drawn gel fibres were 5 to 10 cm average length for both sols with and without water, they were broken to 5 to 10 mm long during drying in the room.

A big difference in appearance was noted between

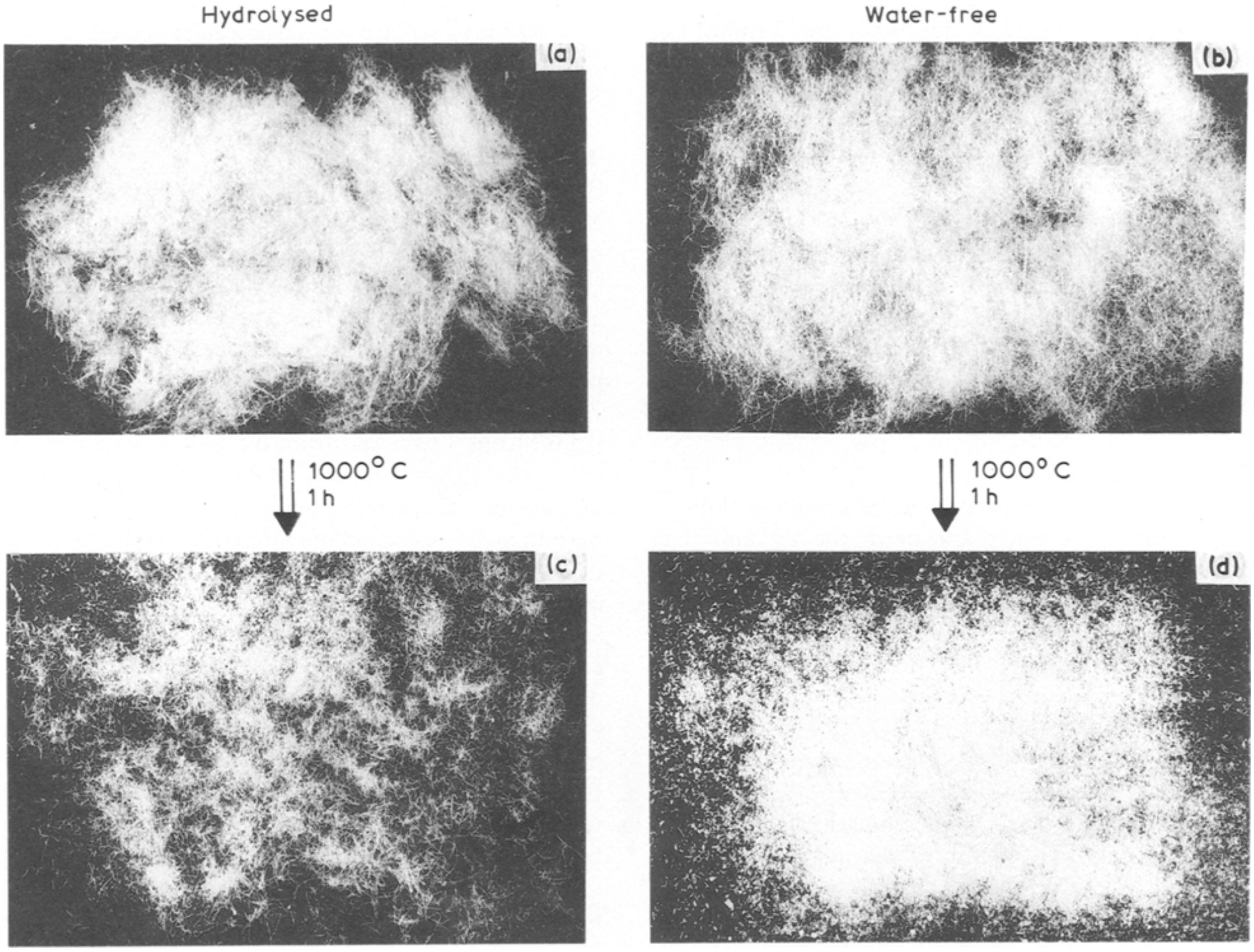


Figure 3 Pictures of BaTiO$_3$ (a) and (b) gel fibres and (c) and (d) ceramic fibres.

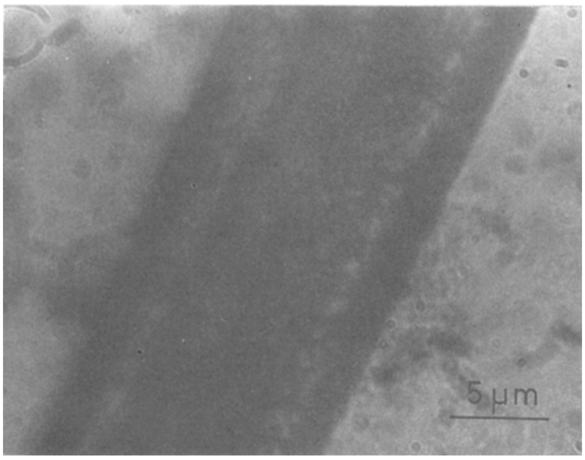


Figure 4 Optical micrograph of BaTiO$_3$ fibres heated at 600° C for 1 h.

heat-treated fibres drawn from the sols with and without water, as clearly seen from Figs 3c and d. That is, the gel fibres drawn from the former sol remained unchanged in shape on heating up to 1000° C, while those from the latter sol were broken and become powdery.

Fig. 4 shows an optical micrograph of BaTiO$_3$ gel fibres heated at 600° C for 1 h. The fibre diameter is about 10 μm. Many cracks are observed on the surface. The fibres heated below 600° C were transparent, while those heated above 700° C were opaque. This is probably due to the occurrence of fine pores by crystallization as shown below.

3.3. Crystallization of the gel fibres

Fig. 5 shows X-ray diffraction patterns of the gel fibres heated at temperatures up to 1300° C for 1 h. The gel fibres heated below 500° C were X-ray amorphous. At 600° C BaTiO$_3$ crystals began to precipitate. No other peaks than those due to BaTiO$_3$ were seen at any temperature up to 1300° C. Variations of the peak intensity and the fwhm of 1 1 1 and 2 0 0 lines with heating temperature are shown in Fig. 6. Both the peak intensities increase with increasing heating temperature due to the crystal growth and improvement of crystallinity, then become almost constant above 1000° C. The fwhms decrease drastically up to 800 or 900° C, then gradually with heating temperature.

These results show that crystallization of the sol–gel derived BaTiO$_3$ gel fibres is completed by heating above 1000° C. However, it is very difficult to judge from these results whether the crystalline form of the precipitated BaTiO$_3$ is cubic or tetragonal, because there is no appreciable increase in the fwhm of the 2 0 0 line which is supposed to split into 2 0 0 and 0 0 2 lines when a cubic form is transformed into a tetragonal one, or vice versa [11].

The crystallite size of BaTiO$_3$ precipitated in the gel fibres heated at several temperatures are plotted against heating time in Fig. 7. At each of the heating temperatures, the crystallite size increases with time and then becomes constant beyond 1 h heating. The higher the heating temperature is, the larger the maximum crystallite size becomes. However, it is interesting to note that the value of 50 nm is still very small.

3.4. Infrared spectra

Fig. 8 shows the infrared spectra of the BaTiO$_3$ gel fibres heated at various temperatures for 1 h. The infrared spectrum of the BaTiO$_3$ gel fibres heated at 100° C has characteristic doublets at 1560 and 1420 cm^{-1}, which are assigned to the asymmetric and symmetric COO vibrations, respectively. There is also a shoulder at 1450 cm^{-1}. From the separation between these, the coordination state of CH$_3$COOH or C$_3$COO$^-$ as a ligand can be inferred to a certain extent [12, 13]. This will be discussed in detail in Section 4. The peak around 1000 cm^{-1} is assigned to Ti–O–C vibration. The absorption peaks at 655 and 620 cm^{-1} may be ascribed to the vibrations of TiO$_6$ octahedra with different types of ligands. A broad band around 800 cm^{-1}, which disappears at higher temperatures, may be due to TiO$_n$ polyhedra with a coordination number of less than 6. At 400° C, the doublet is still

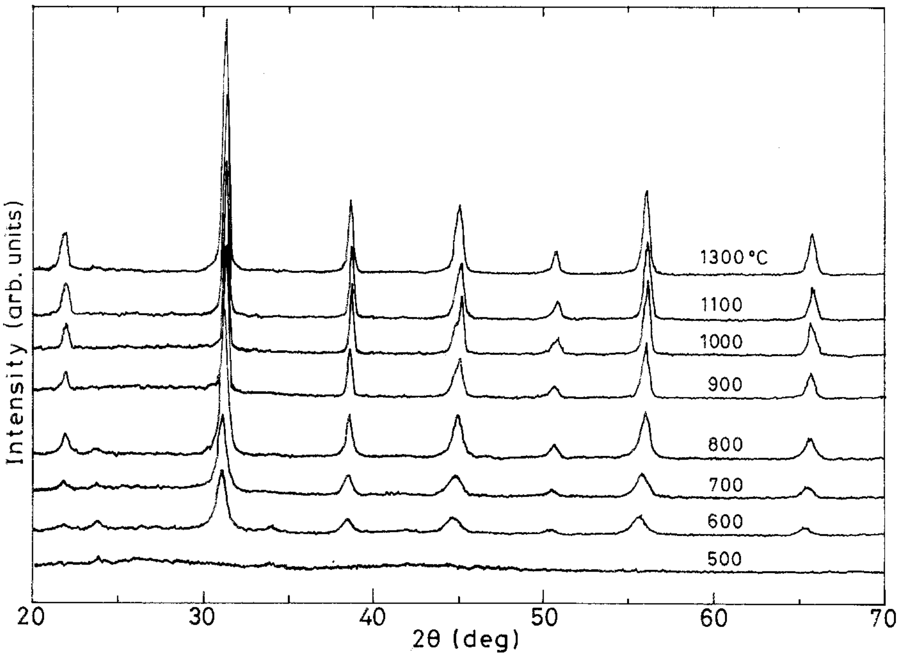


Figure 5 X-ray diffraction patterns of BaTiO$_3$ fibres heated at various temperatures.

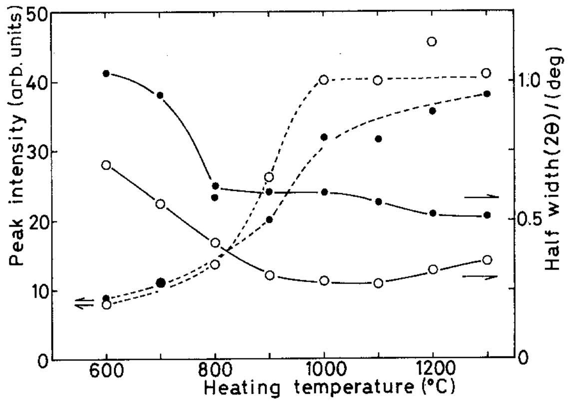


Figure 6 Variations of the peak intensity and the fwhm of (○) 1 1 1 and (●) 2 0 0 lines for $BaTiO_3$ crystal with heating temperature.

visible at 1560 and 1450 cm^{-1}, although no longer clear. Instead, a strong peak appears at 1370 cm^{-1}, which is ascribed probably to the asymmetric stretching vibration of the CO_3 group produced by combustion of the acetyl group. This is ascertained by the presence of the absorption at 860 cm^{-1} (CO_3 out of plane deformation-scissors motion) [14]. A broad band around 600 cm^{-1} suggests the occurrence of TiO_6 octahedra connected to each other above this temperature.

At 600° C, a very strong peak at 1420 cm^{-1} due to CO_3 is observed together with a peak at 860 cm^{-1}. The peak around 600 cm^{-1} becomes very broad. The peaks at 1050 cm^{-1} are no longer seen above this temperature. At 700° C the peak around 600 cm^{-1} becomes deeper. On the other hand, the peak at 1420 cm^{-1} becomes smaller, indicating the decomposition of carbonate groups. At 800° C, no other peaks than that at 560 cm^{-1} due to TiO_6 stretching vibration are seen.

3.5. TG–DTA

Fig. 9 shows TG and DTA curves of the $BaTiO_3$ gel fibres. Three distinct steps of weight loss were observed on the TG curve for the gel fibres. The first is obviously due to vaporization of water and free acetic acid, corresponding to a broad endothermic peak around 100° C on the DTA curve. The second around 250° C involves about 20% weight loss and a small endothermic peak, instantly followed by two large exothermic peaks. Therefore, this step is due to the liberation of alchol and acetic acid from the alkoxide and acetate groups, and their successive combustion. This is also expected from the fact that the fibres heated at 300 to 500° C for 1 h were brown or black in colour.

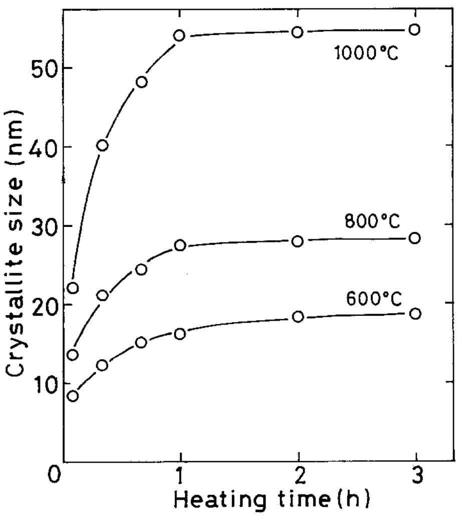


Figure 7 Plots of the crystallite size of $BaTiO_3$ crystal precipitated in the fibres heated at several temperatures.

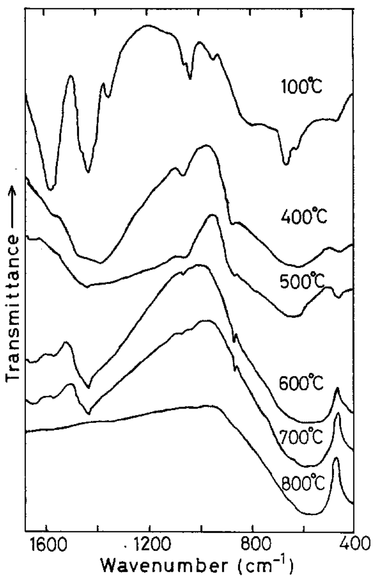


Figure 8 Infrared spectra of the $BaTiO_3$ fibres heated at various temperatures.

The third step around 650° C also accompanies a broad exothermic peak. According to the results of X-ray diffraction, the crystallization of $BaTiO_3$ began at 600° C. Moreover, infrared spectroscopy revealed that carbonate formation occurred above 400° C and decomposed above 700° C. From these results, the third step corresponds to the release of CO_2 gas from the carbonate group and the simultaneous conversion of the amorphous gel fibres into $BaTiO_3$ ceramic ones.

The Curie point of the $BaTiO_3$ gel fibres heated at temperatures from 800 to 1300° C was determined by monitoring the tetragonal–cubic transformation temperature by means of DTA. The results are shown in Fig. 10. For the fibres heated above 1000° C the endothermic peak resulting from this transformation was unambiguously observed, indicating that tetragonal $BaTiO_3$ crystals form on heating the $BaTiO_3$ gel fibres above 1000° C. On the other hand, on heating below 900° C the precipitated $BaTiO_3$ is not a thermodynamically stable tetragonal form, but a

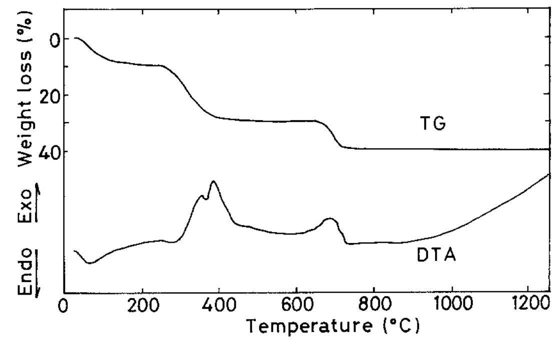


Figure 9 TG–DTA curves of the $BaTiO_3$ gel fibres.

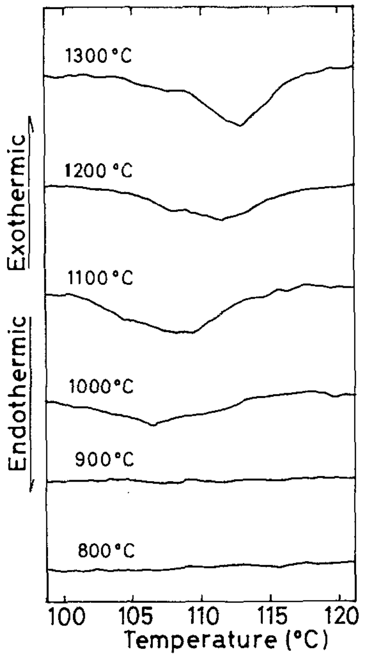


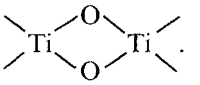
Figure 10 DTA curves of the $BaTiO_3$ ceramic fibres heated at various temperatures.

thermodynamically metastable pseudo-cubic rather than cubic form [11].

In Fig. 11, the Curie point of the $BaTiO_3$ gel fibres heat-treated at temperatures from 1000 to 1300° C is plotted as a function of heating temperature. The Curie point is found to increase linearly with heating temperature.

4. Discussion

According to previous studies [3, 15, 16], the formation of linear polymers in a sol is indispensable for spinnability. For example, the presence of linear polymers consisting of –Si–O–Si– metalloxane bonds has been experimentally confirmed in a spinnable SiO_2 sol prepared by hydrolysis and condensation of $Si(OC_2H_5)_4$ [15–17]. Recently [5] we drew TiO_2 gel fibres from the sol which was prepared with $Ti(O\text{-}isoC_3H_7)_4$, C_2H_5OH, H_2O and HCl as a catalyst and/or a peptizer. The gel fibres thus obtained were successfully converted into the TiO_2 ceramic fibres by heating to 700° C without breaking when the fibre diameter did not exceed several hundred micrometres. This result obviously indicates that the drawn TiO_2 gel fibres consist of linear titanoxane polymers. However, it has not yet been elucidated whether the polymers consist of corner-sharing –Ti–O–Ti– or edge-sharing



.

The sols in the present systems of $Ba(OC_2H_5)_2$–$Ti(O\text{-}isoC_3H_7)_4$–C_2H_5OH–H_2O–CH_3COOH and $Ba(CH_3COO)_2$–$Ti(O\text{-}isoC_3H_7)_4$–H_2O–CH_3COOH were also found to exhibit a spinnability, indicating that some sort of linear polymers should be produced in these sols. In the present case, however, the addition of a large amount of CH_3COOH instead of HCl as a catalyst in the $CH_3COOH/BaTiO_3$ molar ratio of 8 : 12 to the starting solution was required to obtain a clear and spinnable sol. Therefore, it is inferred that the spinnable linear polymers formed in the present sols are not the same as the metalloxane polymers of the type –Ti–O–Ti–.

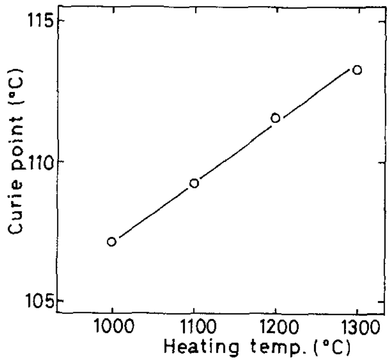
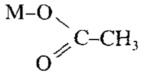
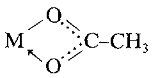
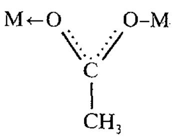
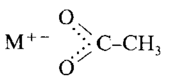


Figure 11 Variation of the Curie point of $BaTiO_3$ ceramic fibres with heating temperature.

Doeuff *et al.* [13] attempted to prepare TiO_2 bulk gels from the $Ti(O\text{-}nC_4H_9)_4$–nC_4H_9OH–H_2O–CH_3COOH mixtures and proposed that CH_3COOH, when added to $Ti(O\text{-}nC_4H_9)_4$, is substituted for the alkoxy group to form a $Ti(O\text{-}nC_4H_9)_{4-x}(CH_3COO)_x$ complex, where x depends on the $CH_3COOH/Ti(O\text{-}nC_4H_9)_4$ molar ratio. With the molar ratio of 2, especially, a stoichiometric compound $Ti(O\text{-}nC_4H_9)_4(CH_3COO)_2$ is found to form. Four types of bonding modes of acetate group to metal ions are possible as depicted in Table I: (a) mono-dentate, (b) chelating, (c) bridging ligands and (d) ionic bond. When the acetate group works as a bridging ligand, $Ti(O\text{-}nC_4H_9)_{4-x}(CH_3COO)_x$ ($x > 2$) forms linear polymers.

The above bonding modes of acetate group can be distinguished from each other to some extent by means of infrared spectroscopy because the infrared spectrum of a carboxylate group, RCO_2^-, shows the characteristic doublet absorption in the wavenumber range 1200 to 1700 cm^{-1} due to the asymmetric and symmetric stretching vibrations of COO (ν_{as}(COO)

TABLE I Symmetric and asymmetric vibrations of carboxylate group (RCO_2^-) with different coordination states after Thile and Panse [12]

	Coordination state	ν_s(COO) (cm^{-1})	ν_{as}(COO) (cm^{-1})	$\Delta\nu$ (cm^{-1})
(a)	 Monodentate	1300	1725	425*
(b)	 Chelating	1435	1565	130*
(c)	 Bridging	1430	1590	160†
(d)	 Ionic	1414 1423	1578 1565	164‡ 142§

*M = Ti; †M = Cu; ‡M = Na; §M = Ba [19]

and ν_s(COO)). The frequency separation between the two peaks strongly depends on the bonding mode as shown in Table I [12, 13], being the largest ($425\,cm^{-1}$) in the monodentate ligand and the smallest ($135\,cm^{-1}$) in the chelating one. Both the bridging and ionic acetate groups take an intermediate value (140 to $160\,cm^{-1}$) which is slightly larger than that of the chelating one, although they are substantially indistinguishable from each other.

Taking into account the present experimental fact that the addition of glacial acetic acid directly to $Ti(O–isoC_3H_7)_4$ gives rise to a spinnable solution, linear $Ti(O–isoC_3H_7)_{4-x}(CH_3COO)_x$ ($x \geqslant 2$) polymers are expected to be present. Accordingly, this means that the use of an amount of acetic acid with the intention of it acting as a catalyst for hydrolysis of metal alkoxide sometimes involves a mechanism very different from the conventional hydrolysis and condensation process as in the system of metal alkoxide–alcohol–H_2O–HCl. This became more striking when a large amount of acetic acid was added. In such a case, acetic acid acts not only as a catalyst, but also as a solvent and a ligand [12, 13].

The infrared spectrum for $BaTiO_3$ gel fibres heated at 100° C shown in Fig. 8 was found to have the well-defined doublet peaking at 1560 and $1420\,cm^{-1}$, and a shoulder at $1450\,cm^{-1}$. Accordingly, the frequency separations between them are 110 and $140\,cm^{-1}$, respectively. This result suggests (1) the absence of monodentate ligand, and (2) the coexistence of at least more than two kinds of acetate groups acting as ligands, chelating ($= 110\,cm^{-1}$) and bridging or ionic ($= 140\,cm^{-1}$), in the $BaTiO_3$ gel fibres heated at 100° C. At this temperature both undecomposed alkoxy and acetate groups are present in the gel. According to Mosset *et al.* [18], barium acetate crystals consist of $Ba_4(CH_3COO)_8$ units, in which acetate groups work mostly as an ionic ligand and one of the two oxygens is further linked to other barium metal. A Fourier transform–infrared study (FT–IR) on $Ba(CH_3COO)_2$ crystals [19] revealed that two types of bonding modes are present whose frequency separations are 135 and $150\,cm^{-1}$, respectively. This results from the coexistence of two kinds of ionic acetate groups with different bond strengths coexisting in the $Ba(CH_3COO)_2$ crystal as easily seen from the crystal structure [18]. However, because these two peaks due to the ν_{as}(COO) are not well separated, conventional infrared spectroscopy gives a broad peak around $1565\,cm^{-1}$ ($\Delta\nu = 142\,cm^{-1}$). Therefore, the doublet with $\Delta\nu = 140\,cm^{-1}$ may be assigned to both the bridging acetate groups of $Ti \leftarrow O–C(CH_3)–O–Ti$ and the ionic acetate groups bonding to barium metal. In the present $BaTiO_3$ gel fibres, $Ba_4(CH_3COO)_8$ units and titanium multinuclear complex [18] do not form, because they could not be detected by X-ray diffraction analysis. Barium ions may be distributed homogeneously over the matrix so that large barium ions may be surrounded by many oxygens octahedrally coordinating to titanium metal in addition to the two acetate groups originally belonging to them.

On heating above 400° C all these peaks are decreased drastically in intensity. In particular, the doublet with $\Delta\nu = 140\,cm^{-1}$ almost disappeared at 400° C. Instead, infrared spectra shown in Fig. 8 indicate the formation of carbonate groups at this temperature. At temperatures between 300 and 400° C both alkoxy and acetate groups coordinating to metal ions decompose and burn as seen from TG–DTA curves (Fig. 9). Because about 30% weight loss was observed at this stage, all of these groups do not result in the formation of carbonate groups. That is, if all the alkoxy and acetate groups are converted into carbonate ones, no weight loss would be observed. From these results, it is considered that only some of the alkoxy and acetate groups are transformed into carbonate groups to form $BaCO_3$. However, as the asymmetric stretching vibration occurred at $1370\,cm^{-1}$, which is much lower than $1420\,cm^{-1}$, and $BaCO_3$ crystal was not observed in the fibres by X-ray diffraction analysis, the coordination state of CO_3^{2-} ions around barium metal is much different from that in the $BaCO_3$ crystal, and $BaCO_3$ does not form aggregates but is dispersed homogeneously as stated above. The bridging acetate groups of $Ti \leftarrow O–C(CH_3)–O–Ti$ is then considered to transform into Ti–O–Ti metalloxane bonds as seen from the facts that the peak at $600\,cm^{-1}$ grows up and is shifted towards lower wavenumbers with heating temperature.

On the contrary, the doublet with $\Delta\nu = 110\,cm^{-1}$ was still visible at 400° C and even persisted up to temperatures as high as 700° C, which is also confirmed from the presence of peaks at 1050 and $2950\,cm^{-1}$ assigned to the Ti–O–C and CH_3 stretching vibrations, respectively. The result shows that the chelating acetate groups coordinating to the titanium atom are both chemically and thermally very stable.

X-ray diffraction analysis (Fig. 5) showed that the crystallization of the gel into $BaTiO_3$ ceramic fibres takes place above 600° C. No other crystals such as $BaCO_3$ and TiO_2 (rutile and anatase) were observed before and after the precipitation of $BaTiO_3$. This also indicates that barium ions are homogeneously distributed in the matrix and Ti–O–Ti linear titanoxane polymers are separated from each other by $BaCO_3$, inhibiting the formation of TiO_2 (rutile or anatase). The precipitation of $BaTiO_3$ crystals occurs just after the decomposition of carbonate groups, which is confirmed by the TG–DTA curves where an obvious weight loss and exothermic peak are observed. From the fact that the Curie point was observed only for the $BaTiO_3$ fibres heated above 1000° C, tetragonal phase $BaTiO_3$ forms above this temperature. The observed Curie points, however, are rather lower than 120° C, which is obtained for a sintered body. This result implies that the $BaTiO_3$ ceramic fibres prepared by the present method have a high degree of residual strain, resulting in a pseudo-cubic crystalline form [11]. This may be closely related to the very fine $BaTiO_3$ crystals precipitated in the fibres as shown in Fig. 7.

5. Conclusion

Multiple oxide $BaTiO_3$ gel fibres were prepared by the sol-gel method mainly from the $Ba(CH_3COO)_2$–$Ti(O–isoC_3H_7)_4$–H_2O–CH_3COOH solutions in the composition range of $4 \leqslant CH_3COOH/[Ba +$

$Ti(O\text{-}isoC_3H_7)_4] \leqslant 7$ and $0 \leqslant H_2O/[Ba + Ti(O\text{-}isoC_3H_7)_4] \leqslant 1$. The added acetic acid was found to replace some of the alkoxy groups to form $Ti(O\text{-}isoC_3H_7)_{4-x}(CH_3COO)_x$, where some of them work as a chelating ligand and one works as a bridging ligand when $x \geqslant 2$. The latter leads to the formation of linear polymers of the type $Ti \leftarrow O\text{-}C(CH_3)\text{-}O\text{-}Ti$ rather than Ti–O–Ti. Addition of water to the solutions seems to break the bridging acetate bonds and replace some of them by bridging oxygen bonds. The as-drawn gel fibres which were X-ray amorphous crystallized into $BaTiO_3$ ceramic fibres upon heating above 600° C. Carbonate formation, probably of $BaCO_3$, was confirmed for fibres heated above 400° C by infrared spectroscopy, but not by X-ray diffraction. This suggests that barium ions are homogeneously distributed in the gel matrix. It is found from the Curie point measurement that the cubic-to-tetragonal transformation takes place on heating above 1000° C.

Acknowledgement

The authors thank Kimiaki Tanaka who assisted in the experiment.

References

1. K. S. MAZDIYASNI, R. T. DOLLOFF and J. S. SMITH II, *J. Amer. Ceram. Soc.* **52** (1969) 523.
2. J. S. SMITH II, R. T. DOLLOFF and K. S. MAZDIYASNI, *ibid.* **53** (1970) 91.
3. S. SAKKA, "Treatise on Materials Science and Technology", Vol. 22 (Academic Press, New York, 1982) pp. 129–67.
4. E. WU, K. C. CHEN and J. D. MACKENZIE, *Mater. Res. Soc. Symp. Proc.* **32** (1984) 169.
5. K. KAMIYA and K. TANIMOTO and T. YOKO, *J. Mater. Sci. Lett.* **5** (1986) 402.
6. K. KAMIYA, T. YOKO, K. TANAKA and H. ITOH, *Yogyo-Kyokai-Shi* **95** (1987) 1157.
7. T. YOKO, K. KAMIYA, K. TANAKA and H. ITOH, Proceedings Sintering '87 Tokyo, edited by S. Somiya, M. Shimada, M. Yoshimura and R. Watanabe (Elsevier Applied Science, London, 1988) pp. 96–101.
8. S. SAKKA, H. KOZUKA and T. UMEDA, *Nippon-Seramikkusu-Kyokai-Gakujutsu-Ronbunshi* **96** (1988) 468.
9. T. UMEDA, H. KOZUKA and S. SAKKA, *Adv. Ceram. Mater.* **3** (1988) 520.
10. D. D. CULLITY, "Elements of X-ray Diffraction", 2nd Edn (Addison Wesley, Reading, MA, 1978) Ch. 3.
11. S. NAKA, M. INAGAKI, Y. SUWA, F. NAKAKITA, A. KAWASHIMA, Y. MASUDA and C. SHIBATA, *Rep. Asahi Glass Found. Indust. Technol.* **22** (1973) 155.
12. K. H. VON THIELE and M. PANSE, *Z. Anorg. Allg. Chem.* **441** (1978) 23.
13. S. DOEUFF, M. HENRY, C. SANCHEZ and J. LIVAGE, *J. Non-Crystal. Solids* **89** (1987) 206.
14. N. B. COLTHUP, L. H. DALY and S. E. WIBERLEY, "Introduction to Infrared and Raman Spectroscopy", 2nd Edn (Academic Press, New York, 1975).
15. S. SAKKA and K. KAMIYA, *J. Non-Cryst. Solids* **48** (1982) 31.
16. K. KAMIYA, T. YOKO and S. SAKKA, *Yogyo-Kyokai-Shi* **92** (1984) 242.
17. D. W. SCHAEFER and K. D. KEEFER, "Better Ceramics Through Chemistry", edited by C. J. Brinker, D. Clark and D. R. Ulrich, (North Holland, New York, 1984) *J. Mat. Soc. Symp.* **32** (1984) 1.
18. A. MOSSET, I. GAUTIER-LUNEAU, J. GALY, P. STREHLOW and H. SCMIDT, *J. Non-Cryst. Solids* **100** (1988) 339.
19. T. UMEDA, H. KOZUKA and S. SAKKA, personal communication.

Received 24 April
and accepted 29 September 1989