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Evolution of the formation of barium titanate in the citrate process: the effect of the pH and the molar ratio of barium ion and citric acid

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In this investigation, several experiments were conducted to study the effects of the molar ratio of barium ion and citric acid and the pH value on the formation of $BaTiO_3$ by the citrate process. It was found that the molar ratio of barium ion and citric acid and the pH value could affect the chelation of carboxylate groups and Ba/Ti ions at temperatures below 450 °C but they seemed not to influence the formation of $BaTiO_3$. The development of an oxycarbonate intermediate during the thermal decomposition of (Ba,Ti) gel was confirmed, which was suggested to possess a structure of $BaTiO_3$, whereby CO_3^{-2} was located inside the layer structure. © *1998 Kluwer Academic Publishers*

1. Introduction

The wet chemical methods for preparing ceramic powders have become increasingly important because they typically lead to high purity and stoichiometric ceramic powders with a fine particle size compared with the solid-state reaction method. These wet chemical methods include sol-gel, coprecipitation, and the citrate process (also called "liquid-mix" or "Pechini" method). However, some problems exist in these methods; e.g. difficult control on the degree of hydrolysis for the desired metal alkoxides in the sol-gel method [1], and inhomogeneous compositional distribution in the coprecipitate when the metal ions have different solubility products or similar ionic sizes [2].

The preparation of barium titanate powder seems to be a very special case in the solution techniques because it can form a complex compound in coprecipitation [3] or a very homogeneous distribution of barium and titanium species on an almost atomic level in the citrate process [4]. However, it is puzzling why an intermediate phase was always observed before the formation of $BaTiO_3$ regardless of the atomic-level mixing of the barium and titanium species [5–11]. Also, due to the existence of the intermediate phase, the temperature for forming $BaTiO_3$ cannot be lowered. Therefore, understanding the mechanism of the intermediate phase development is very important. Two controversial mechanisms [5–11] have been reported for $BaTiO_3$ formation from solution-derived precursors. Some investigations [5–8] have suggested that the precursor might decompose to form highly reactive barium carbonate and titanium (IV) oxide, which subsequently react to form $BaTiO_3$ when heated at 600–700 °C in air. Other reports [9–11] have proposed that an oxycarbonate intermediate might form during the precursor calcination, which then decomposes to $BaTiO_3$. These conflicting propositions could not be resolved as no sharp peaks of either $BaCO_3$ or oxycarbonate intermediate were detected by X-ray diffractometry, possibly due to their poor crystallinity. According to our previous studies [12], the calcining atmosphere and the flow rate play a very important role in the formation of $BaTiO_3$ using the citrate process. It was found that full conversion to $BaTiO_3$ could be achieved when the precursor powder was heated at 475 °C for 1 h at high oxygen flow rate, without the formation of an intermediate phase.

Although the citrate process has been intensively studied, there are several processing parameters deserving further examination to understand the formation mechanism of $BaTiO_3$. According to previous work in the synthesis of a barium ferrite using the citrate process [13], the molar ratio of cations and citric acid and the pH value of the solution would influence the chelation between the cations and the associated citric ions, and affect the thermal decomposition of the precursor powder. In this investigation, photoacoustic Fourier-transform infrared spectroscopy (PA-FTIR) and X-ray diffraction (XRD) were employed to study the effects of the pH and the molar ratio of barium ion and citric ions on the evolution of the formation of $BaTiO_3$ in the citrate process.

2. Experimental procedure

The modified Pechini method [4] was used in this investigation. A titanium solution was prepared by mixing 500 ml of titanium (IV) isopropoxide (97%, Aldrich Chemical, U.S.A.) in 2 l of ethylene glycol (99.5%, GR grade, E. Merck, Germany). 500 g of citric acid monohydrate (99.5%, GR grade, E. Merck, Germany) was then added to this solution, which was stirred and heated until complete dissolution occurred. The resulting clear, yellowish solution was heated subsequently to 90 °C. The content of the titanium ion was determined gravimetrically several times during this process. The barium solution was prepared by dissolving $BaCO_3$ (99.99%, APL Engineered Materials, U.S.A.) in 0.4 M citric solution. The pH value of the mixed (Ba,Ti) solution was adjusted with an ammonia solution (GR grade, E. Merck, Germany). Solutions containing only barium ion, titanium ion, and pure organics were prepared in the same manner. The various solutions were evaporated and stirred on a hot plate at about 80 °C to form a clear (Ba,Ti) gel, barium gel, titanium gel, and pure organic gel.

The photoacoustic Fourier-transform infrared spectra were collected with a 5 kHz rapid-scan at 8 cm^{-1} resolution, using a MTEC Model 200 photoacoustic cell in a BioRad FTS-60A spectrometer. The powder X-ray diffraction patterns were collected on a Siemens D5000 Theta/Theta diffractometer operated at 45 kV and 40 mA with CuK_α radiation.

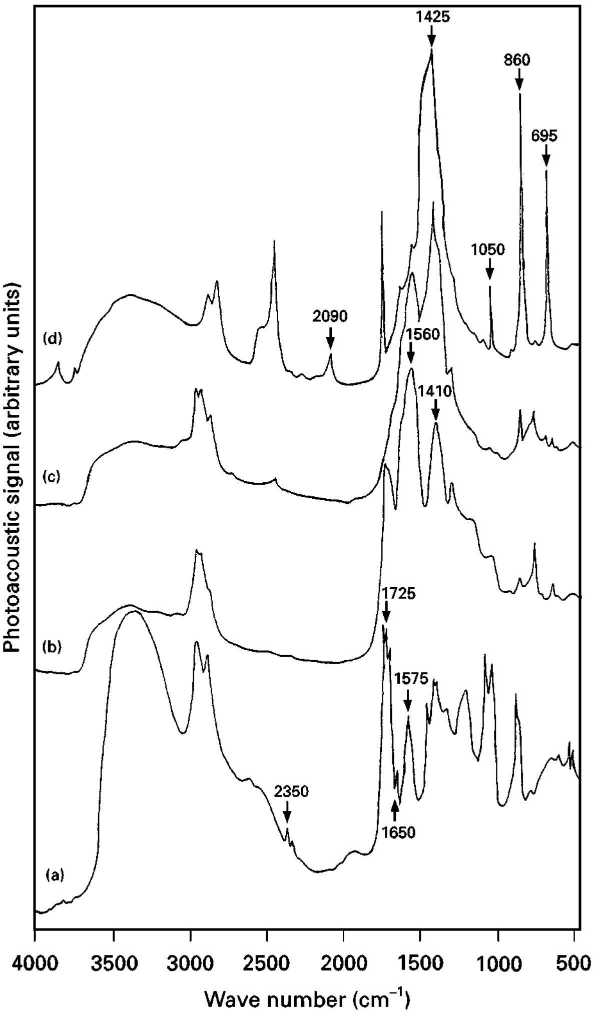

Figure 1 PA-FTIR spectra of (a) the barium gel and the products derived by calcining barium gel at various temperatures: (b) 300, (c) 400, and (d) 450 °C for 0.5 h in air.

3. Results

3.1. The comparison of thermal decomposition behavior of the barium gel, titanium gel, and pure organic gel

The PA-FTIR spectra and the XRD patterns of the barium gel, titanium gel, and pure organic gel and their respective calcined products are illustrated in Figs 1 to 5. Three bands related to carboxylate stretching modes were observed at 1725, 1650, and 1575 cm^{-1} for the barium gel. Because the band at 1725 cm^{-1} was also observed in both titanium gel (Fig. 3a) and pure organic gel (Fig. 5a), this band could be assigned as the C=O stretching mode of the ester which was formed by polymerization of citric acid and ethylene glycol [14]. The 1650 and 1575 cm^{-1} bands of the barium gel and titanium gel could be assigned to asymmetric COO^- stretching mode for a unidentate complex and a bridging complex, respectively [14, 15], formed from the chelation of citric acid and barium or titanium ions. The other infrared bands that were observed at 1500 to 850 cm^{-1} and 3500 to 2800 cm^{-1} were nearly identical for the three different gels and were attributed to the organic network [14] and OH and CH groups [16], respectively. The band at 2350 cm^{-1} was assigned as the symmetric stretching mode of free carbon dioxide [9].

The product derived by heating the barium gel at 300 °C in air for 0.5 h possessed two additional bands at 1560 and 1410 cm^{-1}. These two new bands are typical asymmetric and symmetric stretching

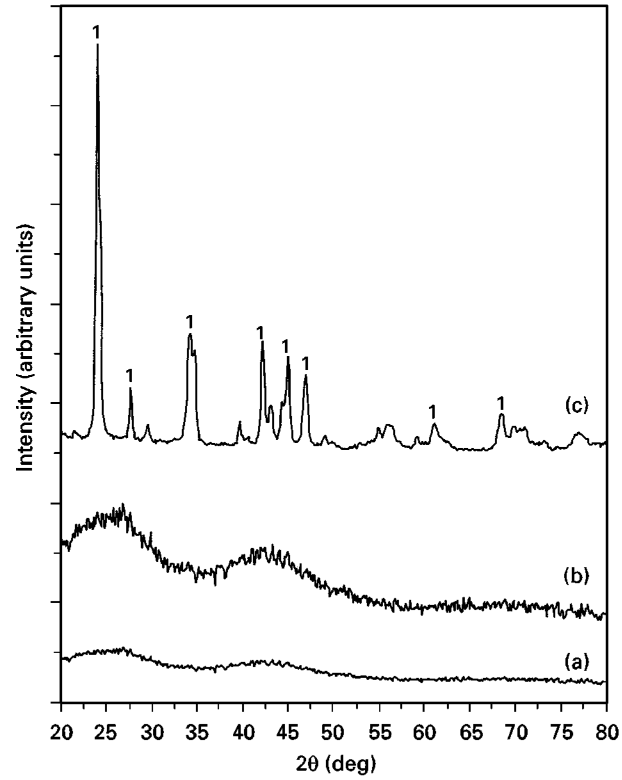

Figure 2 X-ray diffraction patterns of the barium gel calcined at (a) 300, (b) 400, and (c) 450 °C for 0.5 h in air, 1 = $BaCO_3$.

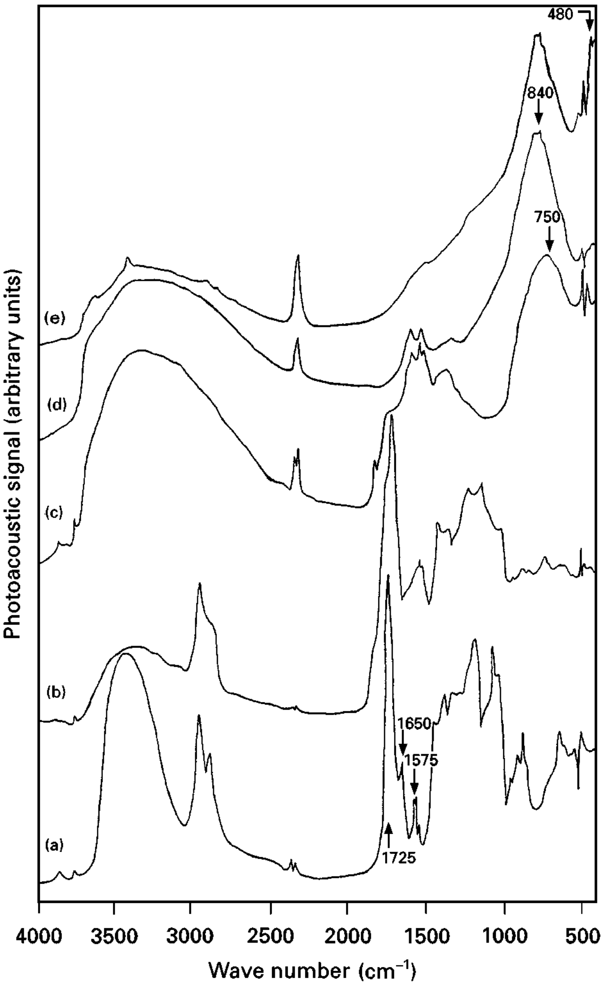

Figure 3 PA-FTIR spectra of (a) the titanium gel and the products derived by calcining titanium gel at various temperatures: (b) 300, (c) 400, (d) 500, and (e) 600 °C for 0.5 h in air.

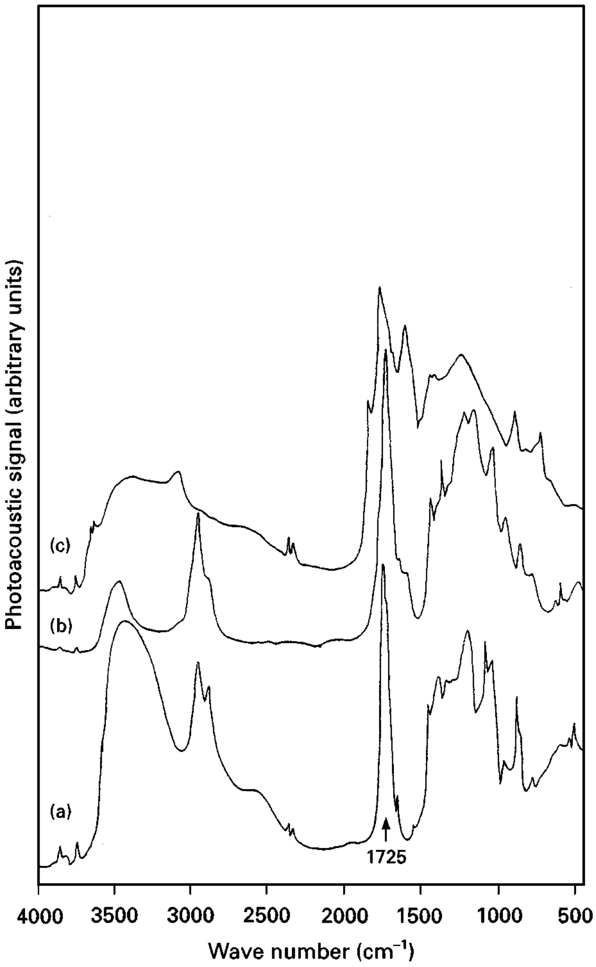

Figure 5 PA-FTIR spectra of (a) the pure organic gel and the products derived by calcining pure organic gel at various temperatures: (b) 300, and (c) 400 °C for 0.5 h in air.

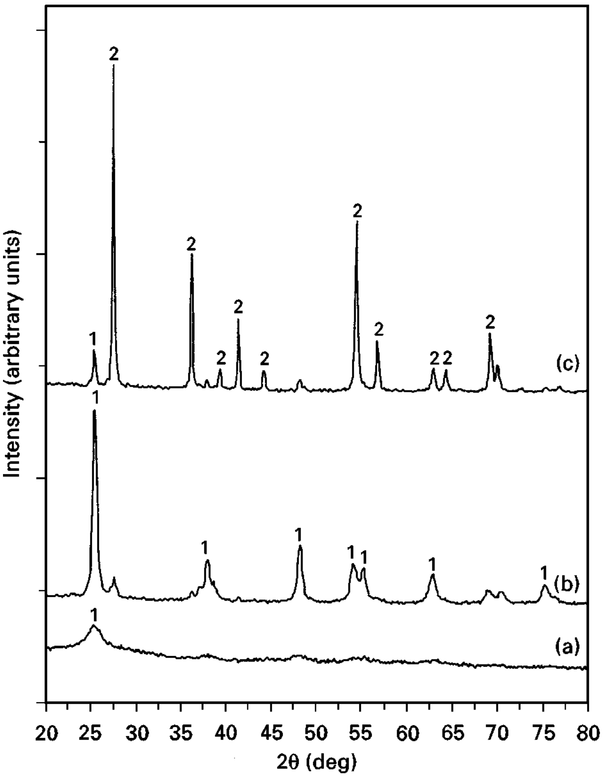

Figure 4 X-ray diffraction patterns of the titanium gel calcined at (a) 400, (b) 500, and (c) 600 °C for 0.5 h in air, 1 = TiO_2 (anatase), 2 = TiO_2 (rutile).

vibrations for carboxylate ions (COO^-) [6, 14] and they were not observed in the titanium system (Fig. 3b). The stretching modes of ester at 1725 cm^{-1} and bridging complex at 1575 cm^{-1} disappeared when the barium gel was heated at 400 °C for 0.5 h. These infrared spectra changes suggested that the nature of bonding between the barium ions and carboxylate groups changed from unidentate complex and bridging complex to ionic bonds by heat treatments and that the evolution of bonding between the titanium ions and carboxylate groups differed from that between barium ions and carboxylate groups.

When the barium gel was heated at 450 °C for 0.5 h, very sharp peaks of 1425, 1050, 860, and 695 cm^{-1} were observed (Fig. 1d), which were attributed to the carbonate ions (CO_3^{2-}) [17]. The XRD pattern of this sample was identified as $BaCO_3$ (Fig. 2c). It should be noted that an additional band at 2090 cm^{-1} which was not observed in titanium gel or commercial $BaCO_3$ powder might be due to the adsorption of carbon monoxide on the surface of $BaCO_3$ powder [18].

Fig. 4a shows that anatase was formed when the titanium gel was heated at 400 °C for 0.5 h. A broad infrared band was found at 750 cm^{-1} which could be

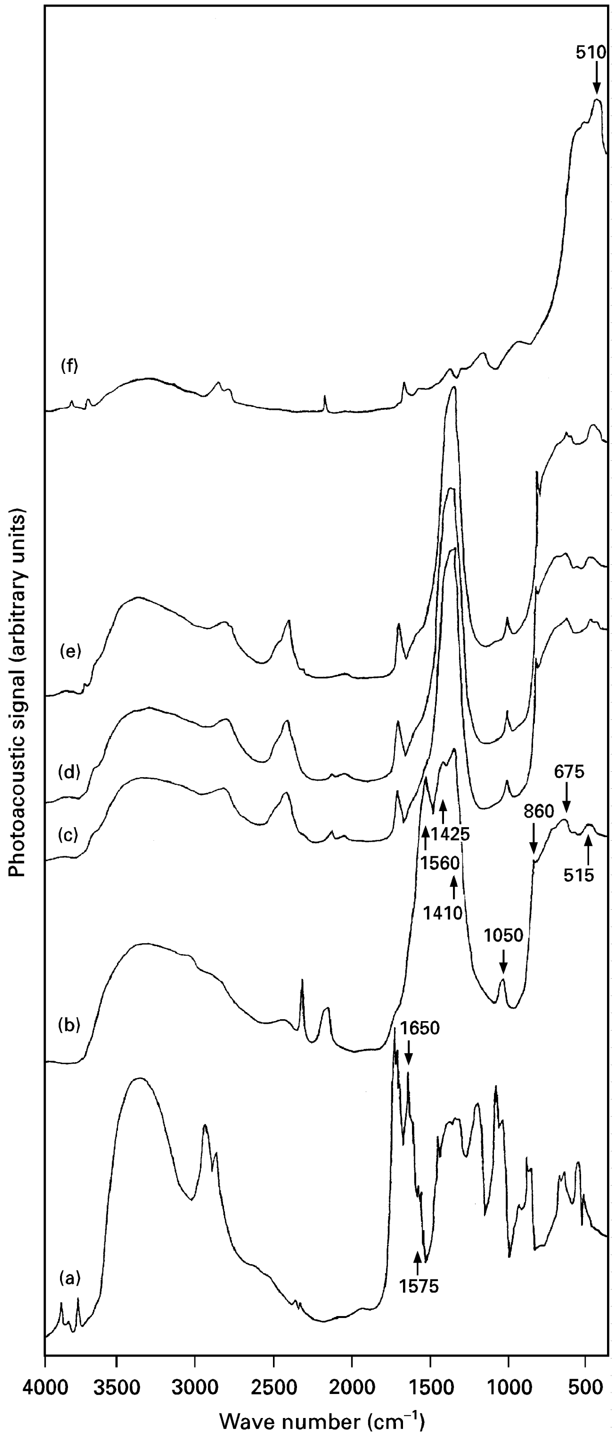

Figure 6 PA-FTIR spectra of (a) the (Ba,Ti) gel with citric acid/Ba = 3 and the products derived by calcining this (Ba, Ti) gel at various temperatures: (b) 450 °C for 0.5 h, (c) 500 °C for 1 h, (d) 500 °C for 2 h, (e) 550 °C for 0.5 h, and (f) 1000 °C for 0.5 h in air.

attributed to the Ti–O stretching mode. No peaks of carbonate ions were observed in the PA-FTIR spectra of differently heat-treated titanium gel in Fig. 3, which agreed with the study of Cho *et al.* [14]. Anatase was formed fully after heating at 500 °C for 0.5 h but the peaks of the Ti–O stretching mode was shifted from 750 cm^{-1} to 840 cm^{-1}. Rutile was observed at 600 °C (Fig. 4c) and an additional infrared band at 480 cm^{-1} (Fig. 3e) appeared which is characteristic of the rutile structure. It should be noted that the peak of 2090 cm^{-1} associated with CO adsorption was not observed in the thermal decomposition of titanium gel.

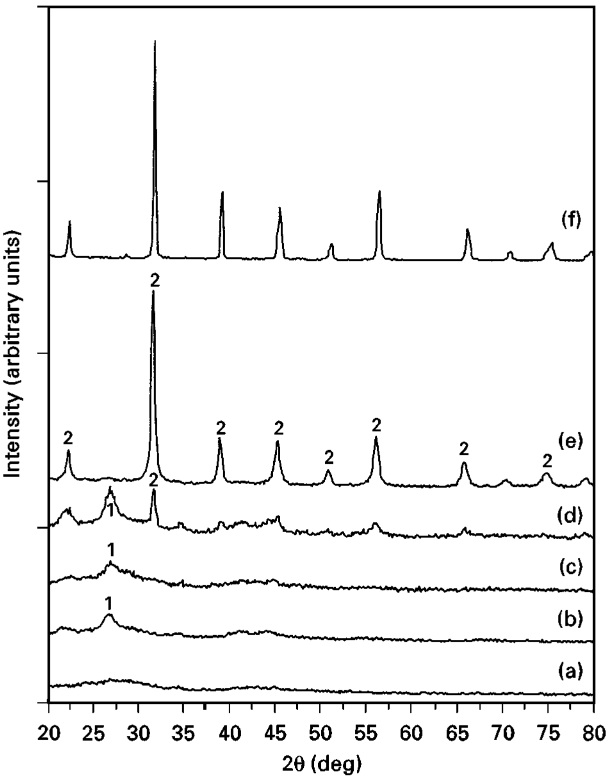

Figure 7 X-ray diffraction patterns of the (Ba,Ti) gel with citric acid/Ba = 3 calcined at (a) 450 °C for 0.5 h, (b) 500 °C for 1 h, (c) 500 °C for 2 h, (d) 550 °C for 1 h, (e) 600 °C for 0.5 h, and (f) 1000 °C for 0.5 h in air, 1 = intermediate, 2 = $BaTiO_3$.

3.2. The effects of the molar ratio of citric acid and barium ion on the formation of $BaTiO_3$

The (Ba,Ti) gels with the molar ratio of citric acid and barium ion of 3, 6, and 12 were calcined at different temperatures for 0.5 h in air. The infrared spectra and the XRD patterns are illustrated in Figs 6 to 11. As observed, the bands related to the organic network and the C=O, O–H, and C–H stretching modes were similar to those of barium gel, titanium gel, and pure organic gel but the relative intensities at 1650 and 1575 cm^{-1} related to the asymmetric COO$^-$ stretching mode of a unidentate complex and a bridging complex were different (Figs 6a, 8a, and 10a). It is interesting to note that the asymmetric COO$^-$ stretching mode of a bridging complex at 1575 cm^{-1} for the (Ba,Ti) gel is stronger for the molar ratio of 6 or 12. It was suggested that the chelation of the cation and the citric ion changed from unidentate to bridging complex when the molar ratio was increased, which is in agreement with the chemical calculation on the concentration of cation citrate complexes in a solution at different conditions [13].

The (Ba,Ti) gels with different molar ratios heated at 450 °C for 0.5 h possessed the peaks related to carbonate ions at 1425, 1050, and 860 cm^{-1} and the peaks related to carboxylate ions at 1560 and 1410 cm^{-1}.

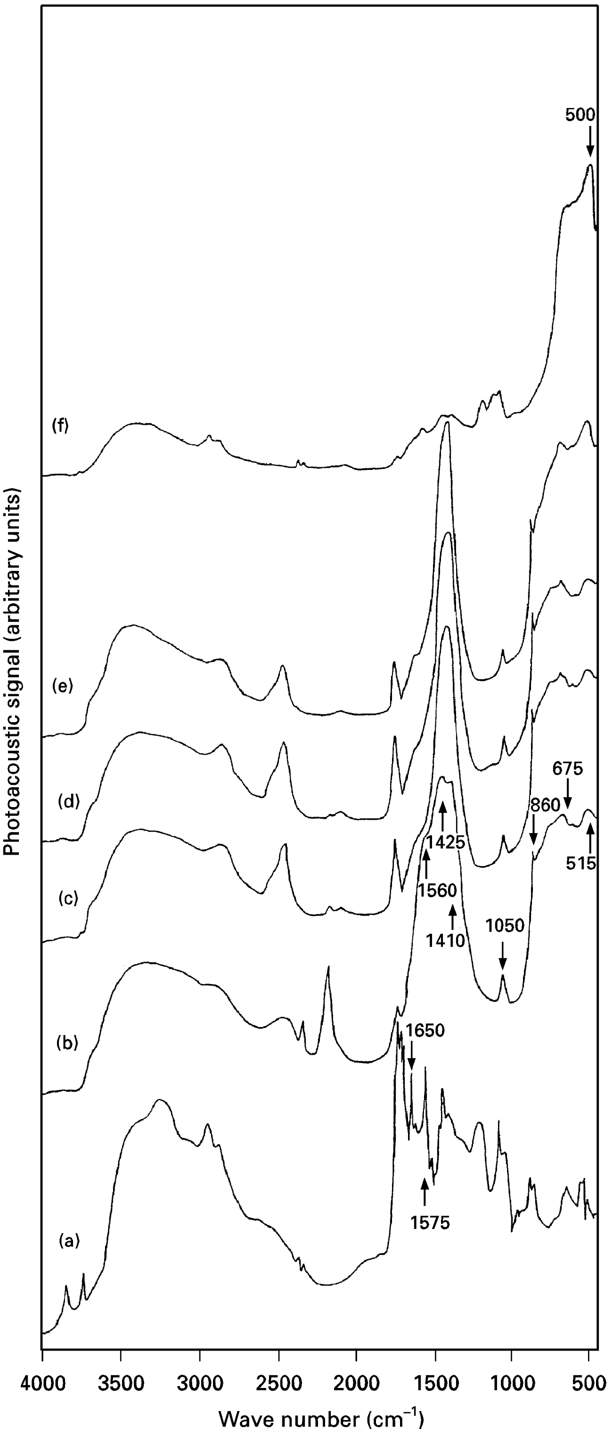

Figure 8 PA-FTIR spectra of (a) the (Ba,Ti) gel with citric acid/Ba = 6 and the products derived by calcining this (Ba,Ti) gel at various temperatures: (b) 450 °C for 0.5 h, (c) 500 °C for 1 h, (d) 500 °C for 2 h, (e) 550 °C for 0.5 h, and (f) 1000 °C for 0.5 h in air.

The band at 675 cm^{-1} could be attributed to a Ti–O stretching mode, although it is shifted a little compared to the pure titania system (Fig. 3c). An additional band observed at 515 cm^{-1} in these three (Ba,Ti) systems could not be assigned to any band of the barium oxide or titania system. The XRD patterns of these three samples showed a broad peak, identified as the oxycarbonate intermediate by Kumar *et al.* [11]. This phase, which was ambiguous in the literature, was clearly observed for the first time in our (Ba, Ti) gels calcined at 500 °C or 550 °C. The infrared spectra of these samples did not change except that the bands related to carboxylate ions at 1560 and 1410 cm^{-1} disappeared. $BaTiO_3$ was formed at 550 °C after 1 h (Fig. 7d and 9d) or at 600 °C after 0.5 h (Fig. 11e), but there were still small amounts of oxycarbonate intermediate and residual $BaCO_3$. The infrared spectra of the single-phase $BaTiO_3$ were shown in Figs 6f and 8f. Although only the oxycarbonate intermediate was detected by XRD, the PA-FTIR spectra showed that the band corresponding to the Ti–O stretching mode at ~510 cm^{-1} was observed in $BaTiO_3$ heated at 450 °C for 0.5 h, suggesting that the Ti–O bond should have been developed in the structure of this intermediate.

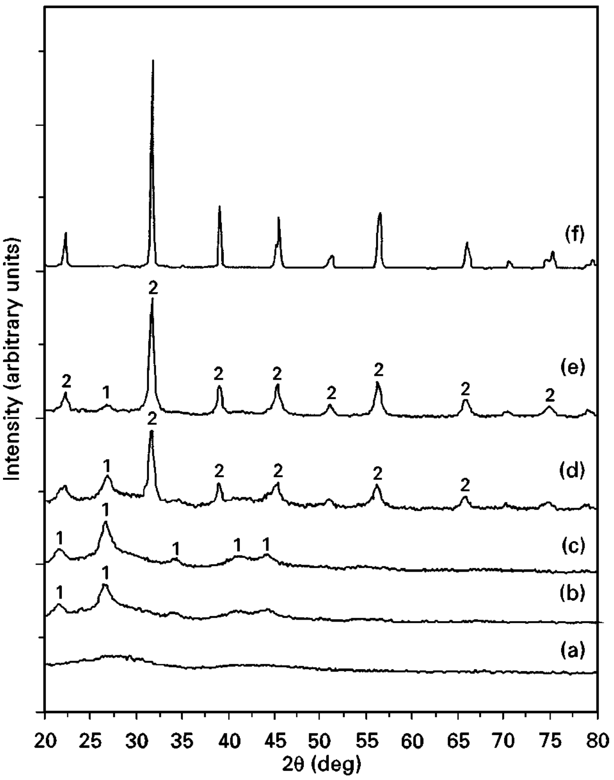

Figure 9 X-ray diffraction patterns of the (Ba,Ti) gel with citric acid/Ba = 6 calcined at (a) 450 °C for 0.5 h, (b) 500 °C for 1 h, (c) 500 °C for 2 h, (d) 550 °C for 1 h, (e) 600 °C for 0.5 h, and (f) 1000 °C for 0.5 h in air, 1 = intermediate, 2 = $BaTiO_3$.

3.3. The effects of the pH value on the formation of $BaTiO_3$

According to our investigation, the higher the molar ratio of citric acid and barium ion in the solution, the larger the pH values could be adjusted without precipitation. Thus, the molar ratio of 12 was selected for studying the effects of pH value on the formation of $BaTiO_3$. Figs 10 to 13 show the PA-FTIR spectra and the XRD patterns of the (Ba,Ti) gels synthesized with pH values of 3 and 9, and their respective calcination products. Comparing Fig. 10a with Fig. 12a, the (Ba,Ti) gel derived with pH = 9 has a more intense band than that with pH = 3 for the asymmetric COO^- stretching mode of a bridging complex at 1575 cm^{-1}, which supports our previous work [13].

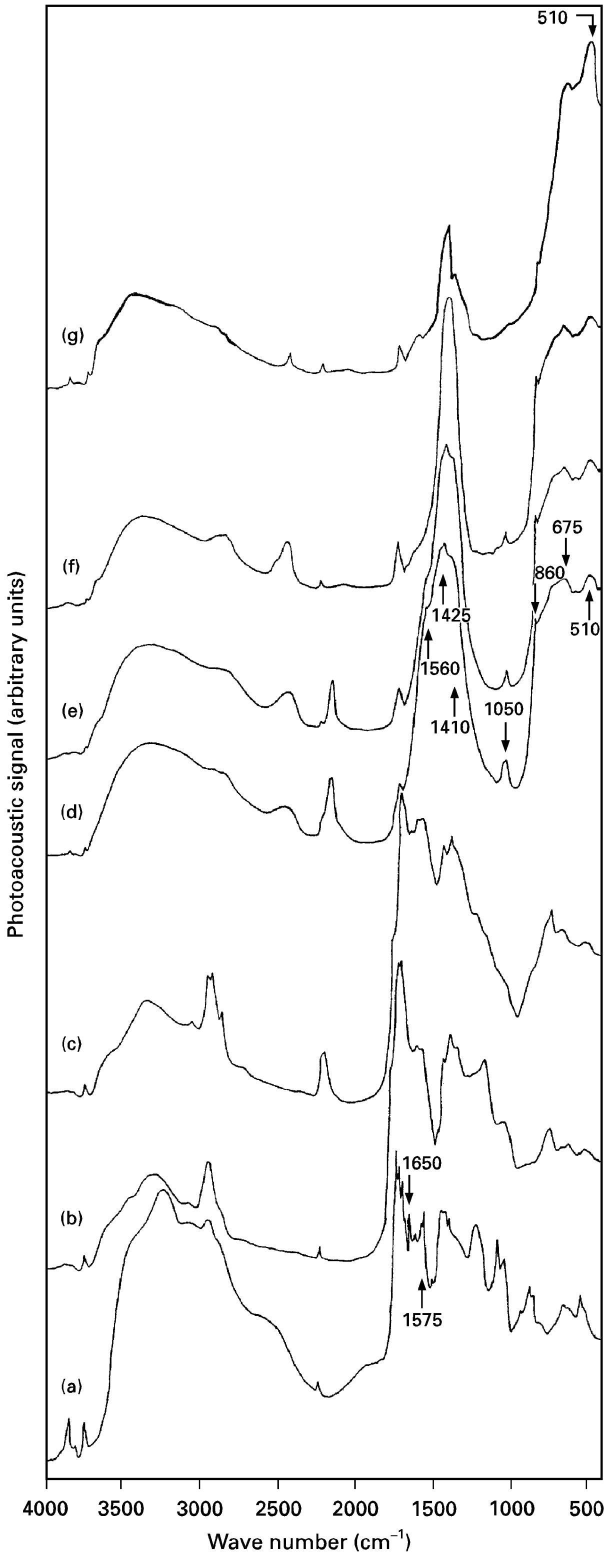

Figure 10 PA-FTIR spectra of (a) the (Ba,Ti) gel with citric acid/Ba = 12 and pH = 3 and the products derived by calcining this (Ba, Ti) gel at various temperatures: (b) 300, (c) 400, (d) 450, (e) 500, (f) 550, and (g) 600 °C for 0.5 h in air.

The PA-FTIR spectra and XRD patterns of these two gels heated above 400 °C are similar to the results in section 2. It suggests that pH value might affect the chelation between the cation and the associated citric ion but has no influence on the formation mechanism of $BaTiO_3$ in the citrate process.

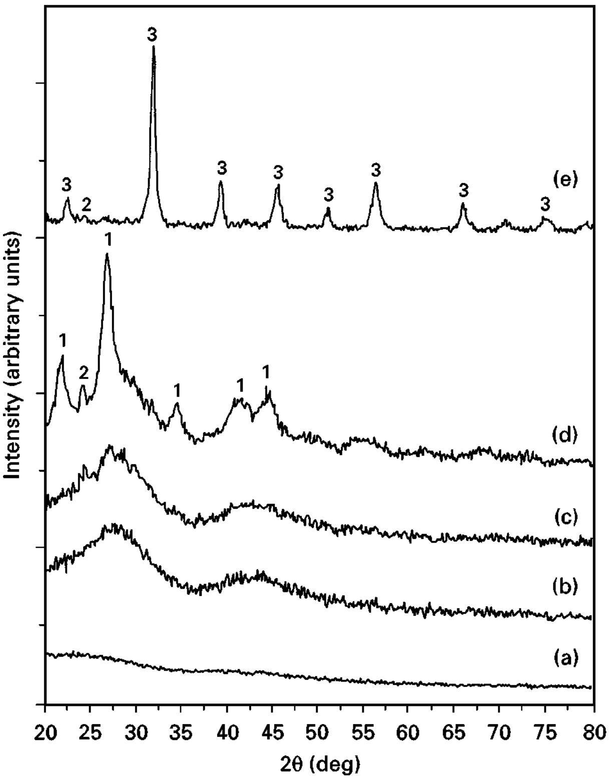

Figure 11 X-ray diffraction patterns of the (Ba,Ti) gel with citric acid/Ba = 12 and pH = 3 calcined at (a) 400, (b) 450, (c) 500, (d) 550, and (e) 600 °C for 0.5 h in air, 1 = intermediate, 2 = $BaCO_3$, 3 = $BaTiO_3$.

4. Discussion

The development of an intermediate phase during the formation of $BaTiO_3$ powder in the citrate process has been in dispute for a long time [5–11]. The ambiguous intermediate phase reported by other researchers is clearly established by XRD (Fig. 11d) in our study. Comparing the infrared spectra of the intermediate phase and $BaCO_3$, there are two distinct differences. Firstly, the bands related to the carbonate ion at 1425, 1050, and 860 cm^{-1} were broader for the intermediate phase than $BaCO_3$. Secondly, the Ti–O stretching mode of $BaTiO_3$ at 510 cm^{-1} was also observed in the spectra of the intermediate phase. Based on these results, it could be inferred that the structure of the intermediate phase might possess the structure of $BaTiO_3$ consisting of CO_3^{2-} within this layered material, which would support the proposition in our recent investigation [12].

5. Conclusion

(1) The molar ratio of barium ion and citric acid and the pH value could affect the chelation of carboxylate groups and cations but they seemed not to influence the formation of $BaTiO_3$

(2) The development of an oxycarbonate intermediate during the thermal decomposition of (Ba, Ti) gel in the temperature range between 450 and 550 °C in air is confirmed, and its structure might be related to a CO_3^{2-} layer development inside the structure of $BaTiO_3$.

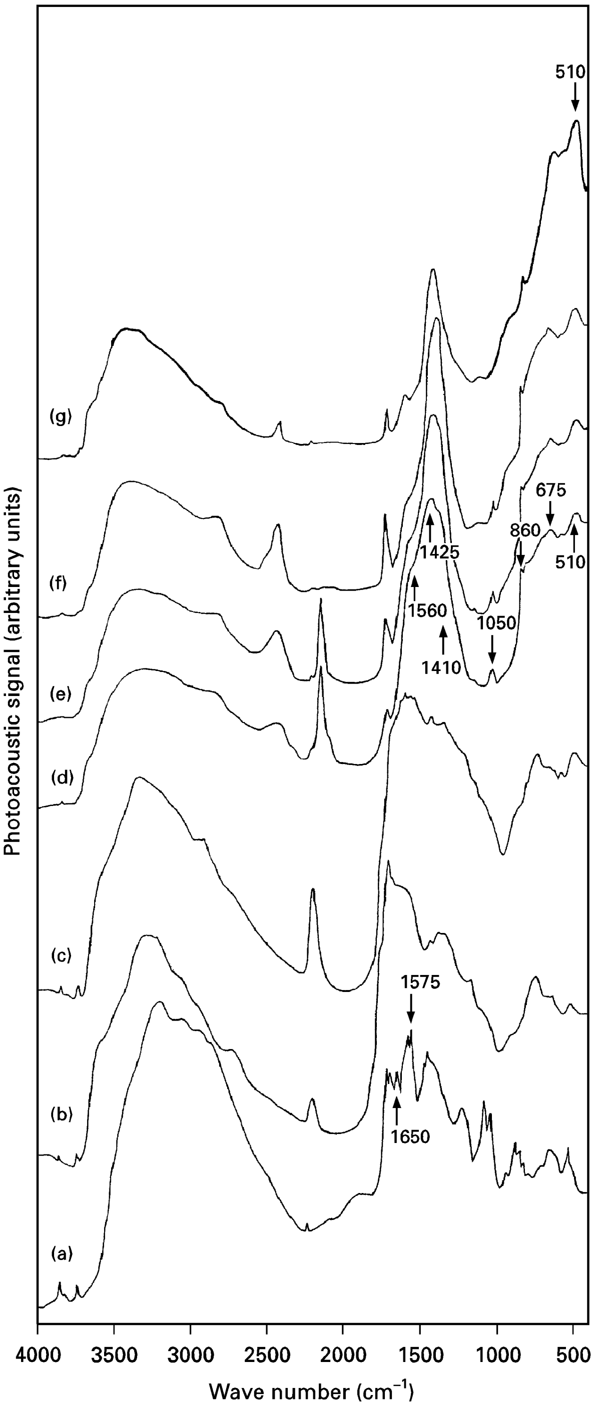

Figure 12 PA-FTIR spectra of (a) the (Ba,Ti) gel with citric acid/Ba = 12 and pH = 9 and the products derived by calcining this (Ba, Ti) gel at various temperatures: (b) 300, (c) 400, (d) 450, (e) 500, (f) 550, and (g) 600 °C for 0.5 h in air.

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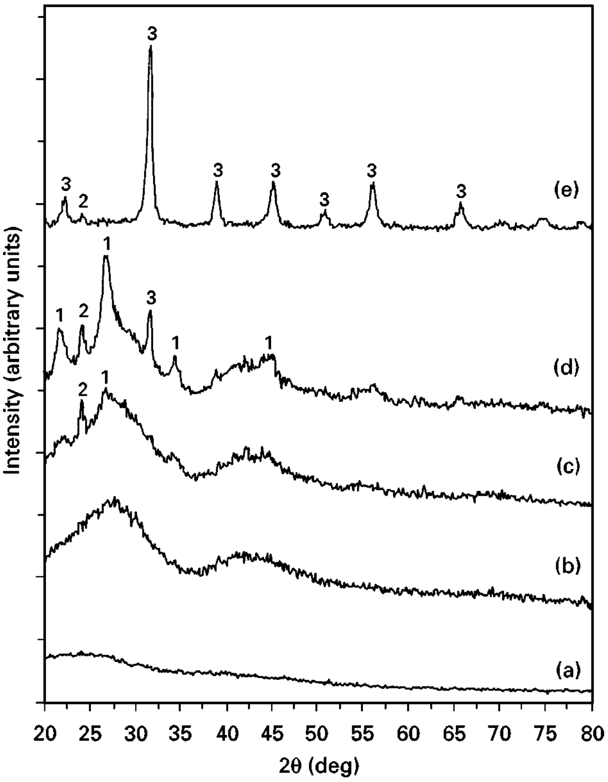

Figure 13 X-ray diffraction patterns of the (Ba,Ti) gel with citric acid/Ba = 12 and pH = 9 calcined at (a) 400, (b) 450, (c) 500, (d) 550, and (e) 600 °C for 0.5 h in air, 1 = intermediate, 2 = $BaCO_3$, 3 = $BaTiO_3$.

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