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# Phase transformation of $TiO_2$ monitored by Thermo–Raman spectroscopy with TGA/DTA

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## Abstract

The advantages of Thermo–Raman spectroscopy are the identification of structure and the ability to monitor the transformation of a sample in a heating process. In this work, Raman spectra were taken continuously from xerogel $TiO_2$ in a heating process similar to that in TGA/DTA. The variation in Raman spectra showed the phase transformation from xerogel to amorphous $TiO_2$ and then to anatase and rutile successively was consistent with the peaks in TGA for a weight loss of 25% at 82°C and two extra endothermic peaks in DTA at 382 and 573°C. However, the transformation from anatase to rutile at 573°C was not complete. © 1997 Elsevier Science B.V.

*Keywords:* Anatase; Rutile; Sol–Gel; TGA/DTA; Thermo–Raman spectroscopy

## 1. Introduction

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) are important in studying the transformation of a solid sample in a thermal process [1]. However, no direct information on the phase transformation can be obtained. Raman spectroscopy has the advantage of identifying the phase of the sample from its vibrational bands. It has been applied to study the changes in structures of superconductors [2]. The Raman spectra were measured to identify the phases or structures at high temperatures [3–7] or to monitor the variation of the phase in a small range of temperature [8–11]. Naturally, the conjunction of these two techniques was suggested [6] or the Raman spectra were measured with TGA simultaneously to identify the transformation in phases [11]. However, the Raman spectroscopy was only used to identify the transformation and not for detailed thermal analysis.

The transformation in the structure and phase of calcium oxalate monohydrate $CaC_2O_4{\cdot}H_2O$, a calibration standard for TGA, was monitored by Raman spectroscopy in a thermal process designed to mimic the TGA/DTA process [12]. This method, Thermo–Raman spectrometry, was used to monitor the transformation in structure or phase by Raman spectroscopy as a function of temperature. Variation in structures in the three temperature intervals corresponding to the three peaks in TGA/DTA was observed. Furthermore, changes in symmetry of $CaC_2O_4{\cdot}H_2O$, $CaC_2O_4$ and $CaCO_3$ were also detected. This work should show some advantages of the Thermo–Raman spectroscopy for thermal analysis.

Titanium dioxide ($TiO_2$) is important for both basic and applied aspects. Its thermal properties [13,14] and

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Raman spectra [4,15–20] have been studied in detail. However, the Raman spectra were always measured at room temperature to identify the structures after being heated to different temperatures [15]. In this work, the phase transformation of xerogel was monitored by Thermal–Raman spectroscopy from 25 to 800°C. The Raman spectra changed as the temperature increased. Variation in Raman spectra indicated successively, the transformation from xerogel to amorphous $TiO_2$, to anatase and then part to rutile. These transformations occurred at various temperatures similar to these TGA/DTA as indicated.

## 2. Experimental

The sample xerogel $TiO_2$ was synthesized by the sol–gel method [21]: $Ti(i\text{-}OPr)_4$ (i-OPr isopropoxy group) in i-PrOH (iso-propanol) was added slowly to i-PrOH with a proper amount of $H_2O$. The composition of the mixture was 1 : 1 : 100 for $Ti(i\text{-}OPr)_4$, $H_2O$ and i-PrOH in molar ratio, respectively. After stirring for 0.5 h and standing for 4 h, it turned into sol then into gel after a longer time. The sol $Ti(i\text{-}OPr)_4$ was partially hydrolyzed to $Ti(OH)_x(i\text{-}OPr)_{4-x}$ with $x \sim 1$. During the aging period, it was hydrolyzed further, then partially condensed and aggregated. Absorption of moisture from the atmosphere promoted hydrolysis and condensation. Blocks of white powdered xerogel formed after evaporation of the volatile components at room temperature. There should be a network structure of $TiO_2$ with some OH and i-OPr groups.

The thermal curves of TGA and DTA were obtained from both freshly prepared and aged xerogel $TiO_2$ using a SEIKO I SSC 5000 thermal gravimetry and differential thermal analysis instrument. The temperature program was set from 25 to 800°C with heating rates of 10 and 20°C $min^{-1}$ in an air flow.

Raman spectra were measured using excitation (30 mW) at a wavelength of 514.5 nm from an argon ion laser (Coherent, Model Innova 100 - 15). The plasma lines in the laser light were removed. The scattered light was collected, dispersed (Spex, 0.5 m spectrometer) and detected by a CCD camera (Princeton Instrument, 1024 × 1024 pixels). The Rayleigh scattered light was reduced by a Notch filter. The sample, a block of xerogel, was placed on a sample holder in the center of a home-made oven. The oven was a piece of stainless steel tubing with four electric heaters inside and a glass window. The temperature was monitored by a thermocouple contacted with the sample holder and controlled by a programmable controller. The uncertainty in temperature reading was about 2°C. The positions of the spectral bands were calibrated using an argon spectral tube. The slit was 50 μm – the resolution was about 6 $cm^{-1}$.

## 3. Results and discussion

### 3.1. *TGA/DTA*

The weight loss curve of the xerogel $TiO_2$ shows only one weight loss of 25% at 82°C in TGA and two extra exothermic peaks at 382 and 573°C in the DTA at a heating rate of 20°C $min^{-1}$ as shown in Fig. 1 [14,15]. The weight loss at 82°C was due to the loss of i-OPr groups from the xerogel during the transformation to amorphous $TiO_2$. Xerogel aged for different periods of time showed different weight losses from 48.3 to 25% at temperatures from 49 to 82°C in TGA. This implied that various amounts of i-OPr groups still bonded to Ti according to the aging period. The peaks around 382 (396°C for a heating rate of 10°C $min^{-1}$) and 573°C did not show any weight loss and should be the phase transformation from amorphous $TiO_2$ to anatase and then to rutile, respectively [14,15]. The

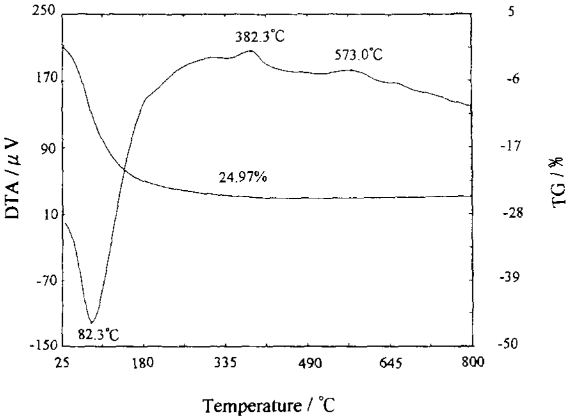

Fig. 1. The thermograms of xerogel $TiO_2$ with a heating rate 20°C $min^{-1}$ in an air flow.

peak at 382°C was only a weak hump but the peak at 573°C was barely distinct and not even detectable at lower heating rate. It is also known that the transformation temperature in DTA depends on many factors, such as sample weight, packing pressure, atmosphere and heating rate, etc.

### 3.2. Raman spectra

Raman spectra of different phases were necessary for the identification of the phases that appeared during the heating process. For $TiO_2$, its Raman spectra are known [4,15–20]. In this work, they were measured from xerogel, aged and after heating to 400 and 700°C for 2 h. The spectra for (a) xerogel or amorphous $TiO_2$, (b) anatase and (c) rutile are shown in Fig. 2 for the range from 94 to 889 $cm^{-1}$. Xerogel had the same spectrum as amorphous $TiO_2$ except a small triplet around 2938 $cm^{-1}$ attributed to the CH stretching mode of the i-OPr group, as shown in Fig. 3.

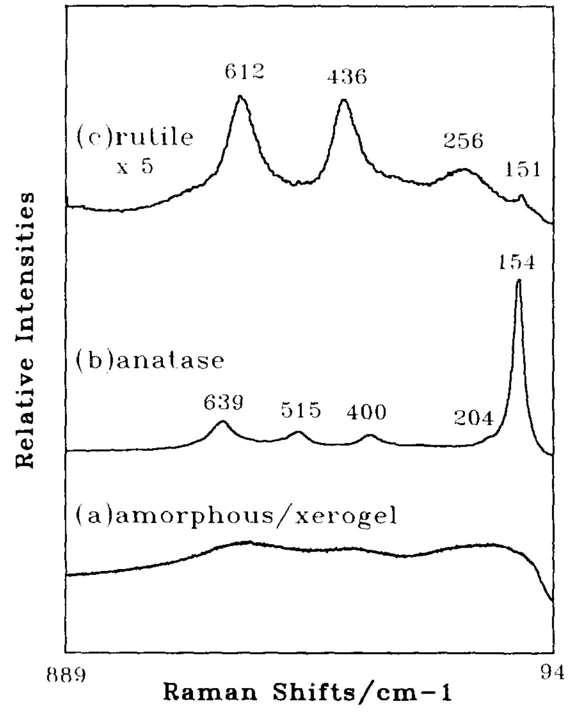

Fig. 2. Three typical Raman spectra for (a) xerogel or amorphous $TiO_2$, (b) anatase and (c) rutile.

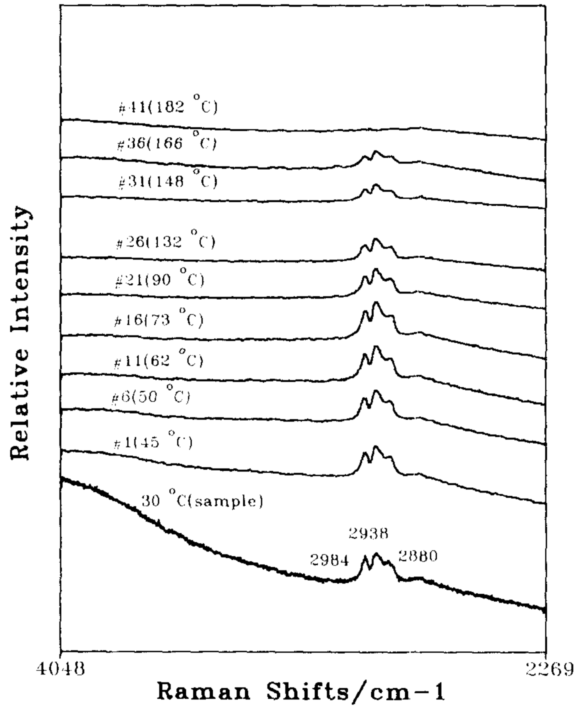

Fig. 3. The Raman spectra from a freshly prepared xerogel for spectra no.1 (45°C) to no.41(182°C). The first spectrum was taken at 30°C before heating .

Amorphous $TiO_2$ had three weak and broad ripples at 171, 422 and 616 $cm^{-1}$ as shown in Fig. 2(a). Anatase had one strong band at 154 $cm^{-1}$ with four weak ones at 204, 400, 515 and 639 $cm^{-1}$ and rutile showed two bands at 436 and 612 $cm^{-1}$ and two weak ones at 256 and 151 $cm^{-1}$, as shown in Fig. 2(b) and (c), respectively. Tables 1 and 2 list the positions of the Raman bands for anatase and rutile, respectively [4,17,18]. Our samples looked

Table 1
Raman bands of anatase ($cm^{-1}$)

| Single crystal [a] | Nanophase $TiO_2$ [b] | This work Fig. 2 | Fig. 11 |
|---|---|---|---|
| 144($e_g$) | 154 | 154 | 143 |
| 197($e_g$) | 205 | 204 | 200 |
| 400($b_{1g}$) | 410 | 400 | 397 |
| 515($b_{1g}+a_{1g}$) | 515 | 515 | 520 |
| 640($e_g$) | 640 | 639 | 637 |

[a] From Ref. [4,18].
[b] From Ref. [17].

Table 2
Raman bands of rutile ($cm^{-1}$)

| Single crystal [a] | Nanophase $TiO_2$ [b] | This work (Fig. 2) |
|---|---|---|
| $143(b_{1g})$ | 154 | 151 |
| 235(mp) | 250 | 256 |
| $447(e_g)$ | 424 | 436 |
| $612(a_{1g})$ | 612 | 612 |

[a] From Ref. [18].
[b] From Ref. [17].

like a nanophase material based on the similarity of the band positions to those given by Parker and Siegel [17,18].

### 3.2.1. *Freshly prepared xerogel*

In order to detect the OH and i-OPr groups, the spectra in the range from 2269 to 4048 $cm^{-1}$ were measured with a time interval of 20 s and an exposure time of 5 s from a freshly prepared xerogel with a heating rate of 10°C $min^{-1}$. Fig. 3 shows the spectra from spectrum no.1 (45°C) to no.41(182°C). The first spectrum was measured at 30°C before the thermal treatment. No stretching mode of OH group was detected which should appear above 3000 $cm^{-1}$. A triplet at 2984, 2936 and 2880 $cm^{-1}$ was observed. It would be the stretching mode of CH bond from i-OPr groups in xerogel. The triplets of $Ti(\text{-i-OPr})_4$ (at 2973, 2929 and 2867 $cm^{-1}$) and i-PrOH (at 2963, 2912 and 2872 $cm^{-1}$) were at different positions. The position of this triplet was higher. This implied that those i-OPr groups were bonded in the network of $TiO_2$. During the heating process, the triplet did not change in position but became weaker in intensity after spectrum no.16 (73°C) and disappeared completely before spectrum no.41(182°C). It changed greatly at spectrum no.21 (90°C). The vanishing of this triplet implied the loss of all i-OPr groups. This could be defined as the transformation from xerogel to amorphous $TiO_2$. There was a large weight loss in the TGA and a big endothermic peak in the DTA for this freshly prepared xerogel. The peak of the weight loss was at 82°C and the weight loss was completed at about 180°C as shown in DTA. The corresponding temperatures were 90°C (spectrum no.21) and 182°C (spectrum no.41) in this Thermo–Raman spectroscopy.

The intensity variation of this triplet was measured by its height and shown in Fig. 4(a) from spectra no.1(45°C) to no.50(212°C). The intensity of i-OPr group increased little at first, decreased slowly until spectrum no.40 (178°C) and then disappeared abruptly. The first increase around spectrum no.14 (69°C) should be the migration of some i-OPr group in the inner part to the surface. The latter decrement indicated the loss of i-OPr groups due to heating and xerogel transformed to amorphous $TiO_2$. The corresponding background was also measured and shown in Fig. 4(b). A decrease in intensity was observed in the first few spectra. This happened in aged sample. Large molecules always show a strong background at the beginning and decrease gradually under irradiation. An increase in background began at spectrum no.33 (155°C), reached a maximum at spectrum no.40 (178°C) and decreased rapidly. The rise and decay in background were at the same pace with the intensity of the triplet band. This phenomenon was also observed in $CaC_2O_4{\cdot}H_2O$ and $CaSO_4{\cdot}2H_2O$ [22]. The rise and decay of the background might indicate the transformation from one phase to another. During

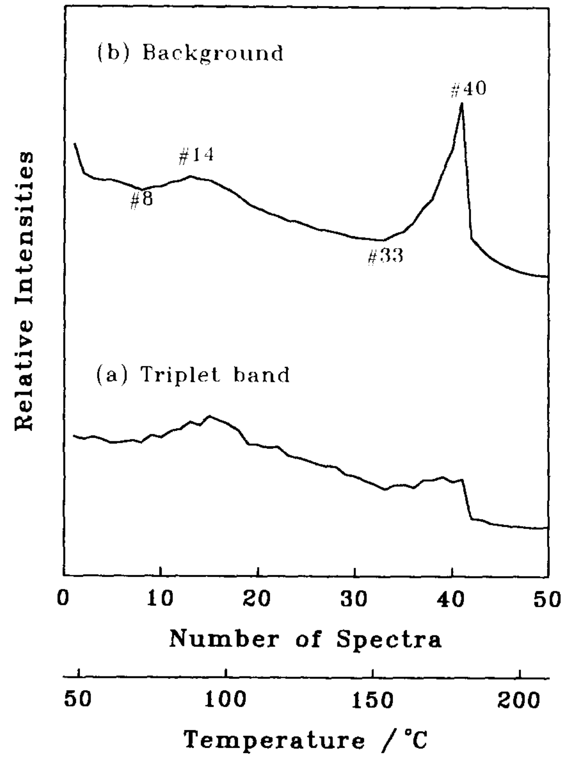

Fig. 4. The intensity variation of (a) the triplet band and (b) the background.

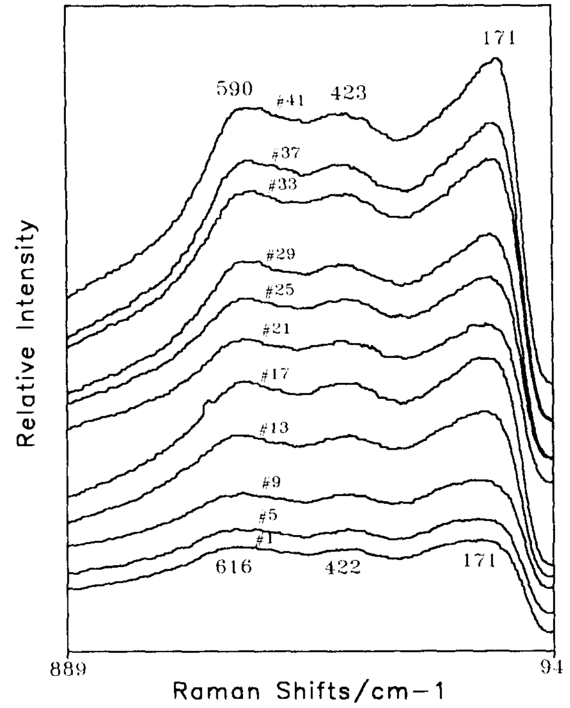

Fig. 5. The Raman spectra from an aged xerogel from spectra no.1 (30°C) to no.41 (371°C).

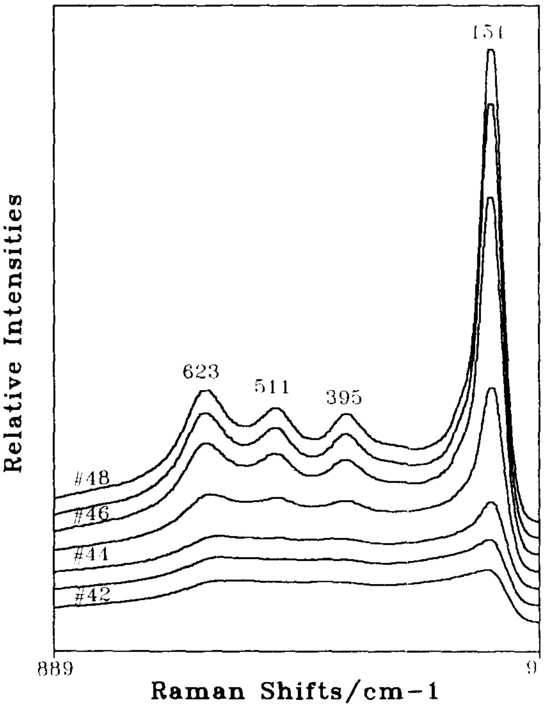

Fig. 6. The Raman spectra from an aged xerogel from spectra no.42(380°C) to no.48(430°C).

the transformation, the atoms in the sample rearranged or disturbed in the solid. This might increase the scattered light. After the transformation the disturbance ceased, the atoms only had thermal motion and the intensity of the scattered light decreased. A similar phenomenon, increase in Rayleigh scattering during the phase transformation of $CaC_2O_4 \cdot H_2O$, was reported by Duval and Condrate [23].

### 3.2.2. *Aged xerogel*

A sample which had been aged for 2 days was heated at a heating rate of 10°C $min^{-1}$ in an air flow. Spectra were taken every 50 s with an exposure time of 2 s. Fig. 5 shows the spectra from spectrum no.1 (30°C) to no.41 (371°C) with every fourth spectrum plotted. All the spectra looked alike except for the broad band at 171 $cm^{-1}$. It became narrower and stronger after spectrum no.9(77°C). This implied that no apparent structural transformation occurred in this temperature range except that the sample became more crystalline. TGA showed a phase transformation from xerogel to amorphous $TiO_2$ around 90°C. These two phases should be similar in structure, therefore no apparent change in the Raman spectra could be observed around 90°C. The spectra from spectrum no.1(30°C) to no.3(39°C) in the range from 91 to 2353 $cm^{-1}$ also showed a reduction in background just as the freshly prepared sample.

### 3.2.3. *Transformation to anatase*

DTA showed the first phase transformation at 382°C. Raman spectra obtained in the temperature range from 380 to 430°C or from spectra no.42 to no.48 are shown in Fig. 6. The main change in the spectrum was the band at 151 $cm^{-1}$. It grew sharper and stronger. Three other weak and broad bands at 395, 511 and 623 $cm^{-1}$ also became stronger. It is the typical spectrum for anatase. This indicated the transformation from amorphous $TiO_2$ to anatase. There was no clear-cut variation in Raman spectra to show this transformation. The band at 151 $cm^{-1}$ grew very rapidly around spectrum no.45. The corresponding temperature was 405°C. It was little higher than 382°C found in DTA.

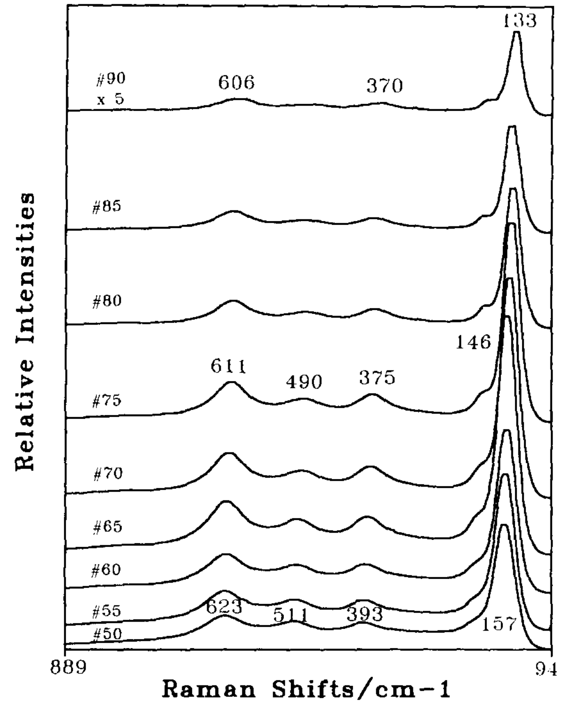

Fig. 7. The Raman spectra from an aged xerogel from spectra no.50 (447°C) to no.90 (780°C).

### 3.2.4. *Transformation to rutile*

The second phase transformation appeared around 573°C in DTA. Spectra no.50 (447°C) to no.90(780°C) are shown in Fig. 7 by plotting every fifth one. The intensity of the band at 151 $cm^{-1}$ increased to a maximum at spectrum no.65 (572°C) and then decreased to nearly vanish by spectrum no.90 (780°C). The position of that band shifted to 146 $cm^{-1}$ at spectrum no.75(655°C) and further to 133 $cm^{-1}$ at spectrum no.90 (780°C). In the meantime, the bands at 393, 511 and 623 $cm^{-1}$ behaved similarly. They shifted to 375, 490 and 611 $cm^{-1}$ at spectrum no.75 (655°C). These shifts in band positions might indicate a change in oxygen contents or the crystallinity. The decrease in intensity of the band at 151 $cm^{-1}$ might indicate the beginning of the transformation of anatase to rutile. Another possibility was the reduction in intensity of anatase at high temperature [22]. Finally, the spectrum became very weak as the spectrum no.90 (780°C) (enlarged by 5) showed. Raman bands for both anatase and rutile became very weak and nearly undetectable at high temperature [22]. This part was under investigation.

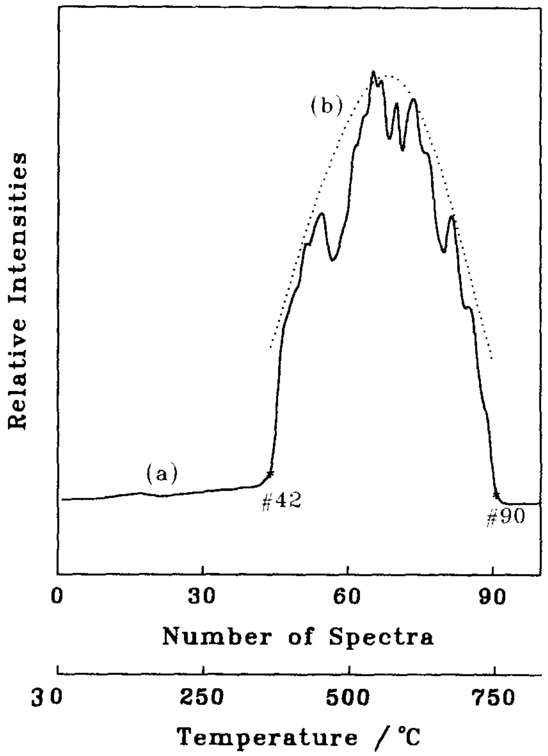

Fig. 8. The intensity variation (area) of (a) the Raman band at 151 $cm^{-1}$ and (b) after smooth by covering the humps.

The intensity of the band around 151 $cm^{-1}$ was measured and plotted in Fig. 8(a). It represented the amount of anatase. It appeared at spectrum no.42 (380°C), reached a maximum at spectrum no.67 (588°C), and nearly vanished by spectrum no.90 (780°C). Several humps, which might be caused by the readjustment of the camera lens due to the off-alignment, appeared as the temperature was raised. The real variation might be represented by a smooth curve which covered those humps as curve (b). Apparently, the xerogel experienced a sequence reaction in this heating process as follows:

$$\text{Xerogel} \rightarrow \text{Amorphous TiO}_2 \rightarrow \text{Anatase} \rightarrow \text{Rutile}$$

Xerogel transformed to amorphous $TiO_2$ completely at a temperature around 180°C. The variation of the intensity of the band at 151 $cm^{-1}$ was the largest around 90°C. It was between 49–82°C as in TGA. Anatase appeared at spectrum no.42 (380°C). The intensity increased fast at spectrum no.45 (405°C) that might correspond to the peak at 382°C in DTA. Its intensity reached a maximum at spectrum no.67 (588°C) then decreased to nearly vanish. The sample was cooled to room temperature and a spectrum of a mixture of anatase and rutile was observed with the anatase as the major component. This indicated that the transformation from anatase to rutile might start at spectrum no.67 (588°C) but was not complete even when heated up to 800°C. An endothermic peak in the DTA was observed at 573°C with several weak and broad ripples appearing at higher temperatures. The peak at 573°C could correspond to a transformation of a part of anatase to rutile and the ripples might indicate that the transformation was still in progress.

### *3.2.5. Thermo–Raman spectroscopy*

From the above results, the phases presented at various temperatures could be identified directly from the Raman spectra by comparing with the spectra of known structures or monitored by Raman spectroscopy in a heating process. This is Thermo–Raman spectroscopy which shows the variation in Raman spectra as a function of temperature. It can provide some evidence for the transformation in thermal analysis.

Its advantages functioned in this work were: (1) the identification of the structure; (2) the ability to monitor the transformation in sample in situ by a CCD camera within seconds; (3) the rise and decay of the background which probably indicates the formation of a new phase or a new compound; (4) both the appearance and the disappearance of one phase; and (5) only small amount of sample needed.

However, it showed following disadvantages in this work: (1) difficulties caused by the weakness of the Raman bands of anatase and rutile at high temperature: (2) error in temperature measurement caused by the heating effect from the laser irradiation. However, it would be small in white solid under the irradiation of low laser power; (3) difficulties in sampling from inhomogeneous sample, and (4) impossibility in probing the inner part of non-transparent samples.

## 4. Conclusion

In this work, Thermo–Raman spectroscopy was used to monitor the phase transformation of xerogel to amorphous $TiO_2$, anatase and rutile in a thermal process. The amorphous $TiO_2$ had only weak Raman bands. Anatase showed one strong Raman signal and was easy to monitor. Unfortunately, rutile did not have distinct signal at high temperature. However, three transformations could be observed.

A freshly prepared xerogel showed a triplet band of i-OPr groups. The transformation to amorphous $TiO_2$ was indicated by the vanish of that triplet band around 180°C. In an aged xerogel this transformation was not distinct as the Raman spectra were similar. However, some minor changes in spectra were observed. Amorphous $TiO_2$ transformed to anatase by the appearance of a strong band at 151 $cm^{-1}$ . Rutile did not show strong Raman band at high temperature for identification. Its presence was revealed by the bands at 612 and 412 $cm^{-1}$ after being cooled to room temperature. However, this transformation was not complete even when heated to 800°C. The corresponding peak at 573°C should indicate the transformation of anatase partially to rutile. The ripples followed might indicate that the transformation was still in progress as shown in DTA.

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## References

[1] W.W. Wendlandt, Thermal Analysis, John Wiley, New York, (1986).

[2] H. Chang, Q. Xiong, Y.Y. Xue and C.W. Chu, Physica C, 248 (1995) 15.

[3] R.G. Herman, C.E. Bogdan, P.L. Kumler and D.M. Nuszkowski, Mater. Chem. Phys., 35 (1993) 233.

[4] E. Haro-Poniatowski, R. Rodriguez-Talavera, M. de la Cruz Heredia, O. Cano-Corona and R. Arroyo-Murillo, J. Mater. Res., 9 (1994) 2102.

[5] P.K. Dutta, P.K. Gallagher and J. Twu, Chem Mater., 5 (1993) 1739.

[6] P.K. Dutta, P.K. Gallagher and J. Twu, Chem. Mater., 4 (1992) 847.

[7] E. Kestila, M.E.E. Harju and J. Valkonen. Thermochim. Acta, 214 (1993) 67.

[8] D. Duval, Sr. and R.A Condrate, Appl. Spectrosc., 42 (1988) 701.

[9] Y.J. Jiang, L.Z. Zeng, R.P. Wang, Y. Zhu and Y.L. Liu, J. Raman Spectrosc., 27 (1996) 31.

[10] I. Noiret, A. Hedoux, Y. Guinet and M. Foulon, Europhys. Lett., 22 (1993) 265.

[11] M.E.E. Harju, Appl. Spectrosc., 47 (1993) 1926.

[12] H. Chang and P.J. Huang, Anal. Chem., 69 (1997) 1485.

[13] J.I. Keddie, P.V. Braun and E.P. Giannelis, J. Am. Ceram. Soc., 77 (1994) 1592.

[14] W.F. Sullivan and S.S. Cole, J. Am. Ceram. Soc., 42 (1959) 127.

[15] D. Bersani, P.P. Lottici, M. Braghini and A. Montenero, Phys. Stat. Sol. (b), 170 (1992) K5.

[16] Y.H. Chee, R.P. Cooney, R.F. Howe and P.A.W. van der Heide, J. Raman Spectrosc., 23 (1992) 161.

[17] J.C. Parker and R.W. Siegel, Appl. Phys. Lett., 57 (1990) 943.

[18] J.C. Parker and R.W. Siegel, J. Mater. Res., 5 (1990) 1246.

[19] R.W. Capwell, F. Spagnolo and M.A. DeSesa, Appl. Spectrosc., 26 (1972) 537.

[20] G.A. Tompsett, G.A. Bowmaker, R.P. Cooney, J.B. Metson, K.A. Rodgers and J.M. Seakins, J. Raman Spectrosc., 26 (1995) 57.

[21] B.C. Jeffrey and G.W. Scherer, Sol–Gel Science, The Physics and Chemistry of Sol–Gel Processing, Academic Press, Boston, (1990).

[22] H. Chang and P.J. Huang, unpublished.

[23] D. Cuval and R.A. Condrate, Sr, Phys. Stat. Sol. (b), 132 (1985) 83.