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# Low-temperature synthesis, pyrolysis and crystallization of tantalum oxide gels

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Tantalum oxide gels in the form of transparent monoliths and powders have been prepared from hydrolysis of tantalum pentaethoxide under controlled conditions using different mole ratios of $Ta(OC_2H_5)_5:C_2H_5OH:H_2O:HCl$. Alcohol acts as the mutual solvent and HCl as the deflocculating agent. For a fixed alkoxide:water:HCl ratio, the time of gel formation increased with the alcohol to alkoxide molar ratio. Thermal evolution of the physical and structural changes in the gel has been monitored by differential thermal analysis, thermogravimetric analysis, X-ray diffraction, and infrared spectroscopy. On heating to ~ 400 °C, the amorphous gel crystallized into the low-temperature orthorhombic phase $\beta$-$Ta_2O_5$, which transformed into the high-temperature tetragonal phase $\alpha$-$Ta_2O_5$ when further heated to ~ 1450 °C. The volume fraction of the crystalline phase increased with the firing temperature. The $\alpha$-$Ta_2O_5$ converted back into the low-temperature phase, $\beta$-$Ta_2O_5$, on slow cooling through the transformation temperature of 1360 °C, indicating a slow but reversible transformation.

## 1. Introduction

$Ta_2O_5$ films have received attention [1] recently for applications as storage capacitors in very large-scale integrated memory cells and as a gate insulator in MOS devices because of their large dielectric constant. Tantalum oxide dielectric films are also frequently used [2] in display technologies, such as thin-film electroluminescence and thin-film transistor liquid-crystal displays. $Ta_2O_5$ thin films have also been used for optical waveguides [3, 4] and antireflection coatings [5] on solar cells due to the high chemical stability of this oxide and its optimum optical properties, such as a high refractive index and a very low absorption coefficient for light. $Ta_2O_5$ films have also been used as solid-state oxygen sensors [6] because of their high ionic conductivity. $Ta_2O_5$ coatings deposited [7] from tantalum pentaethoxide solutions using the sol–gel technique, are also being investigated [7] as interfacial barrier layers to prevent chemical interaction between high-temperature superconductor $YBa_2Cu_3O_{7-x}$ films and ceramic substrates. Because of its excellent chemical stability and high thermal stability, $Ta_2O_5$ may also be useful as compliant/protective layers for the fibre–matrix interface in fibre-reinforced ceramic–matrix composites which are being developed for use as high-temperature structural materials in advanced high-efficiency, high-performance engines.

$Ta_2O_5$ is the only thermodynamically stable oxide of tantalum [8, 9]. It exists in two crystallographic forms, a low-temperature orthorhombic phase, termed $\beta$- or L-$Ta_2O_5$, and a high-temperature tetragonal phase, called $\alpha$- or H-$Ta_2O_5$. The transformation occurs reversibly and slowly at ~ 1360 ± 10 °C [8]. In addition, several metastable polymorphic modifications have been reported [10–12].

The objective of the present work was to synthesize tantalum pentoxide by the sol–gel technique and to study the thermal evolution of the gel structure. Transparent monolithic and powder gels have been prepared from the hydrolysis of tantalum pentaethoxide under various experimental conditions. The structural changes occurring in the gel as a function of heat-treatment temperature have been investigated using differential thermal analysis, thermogravimetric analysis, X-ray diffraction, and infrared spectroscopy.

## 2. Experimental procedure

Tantalum ethoxide, $Ta(OC_2H_5)_5$, from Alfa Products and 200 proof ethyl alcohol were used without any further treatment. The relative amounts of various chemicals used are given in Table I. The handling of $Ta(OC_2H_5)_5$ was carried out inside a glove box because of its high reactivity with atmospheric moisture. After appropriate quantities of tantalum pentaethoxide and ethanol were mixed, the container was sealed with parafilm and taken out of the dry box. A 50 % (vol/vol) HCl solution (prepared by mixing equal volumes of concentrated hydrochloric acid and water) was then slowly added dropwise with a burette under brisk stirring. A homogeneous clear solution having a light-yellow colour resulted. The sealed containers were stored under ambient conditions to allow completion of the alkoxide hydrolysis and polymerization reactions. It took anywhere from a few hours to several days for gel formation, depending upon the relative concentrations of the various reactants in the solution. A few holes were punched in the parafilm and the gels were allowed to dry slowly under ambient conditions. Clear, transparent, and monolithic dry gel in the form of discs of ~ 2 cm diameter and ~ 0.4 cm thick were obtained, as shown in Fig. 1.

A large batch of the gel was prepared using 51.8 g tantalum pentaethoxide, 150 ml ethanol, and 5.0 ml aqueous 50 % HCl (vol/vol) solution. The gel was allowed to dry for approximately 8 weeks under ambient conditions resulting in porous bulk pieces which were stored in a sealed container until used for further treatment and characterization. This gel will henceforth be referred to as "TA".

The dried gel powder was subjected to various thermal treatments at temperatures between 110 and 1450° in air in a platinum crucible. Thermal evolution of gel structure was monitored using various techniques. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed using Perkin–Elmer DTA-1700 and TGS-2 systems, respectively, which were interfaced with computerized data acquisition and analysis systems. Infrared (IR) transmission spectra were recorded in the range 4000–450 $\text{cm}^{-1}$ using the KBr pellet method with a Perkin–Elmer 1750 Infrared Fourier Transform Spectrometer interfaced with a Perkin–Elmer 7300 professional computer. Powder X-ray diffraction (XRD) patterns were collected at room temperature using a step-scan procedure (0.03 °/2θ step; count time 0.5 s) in the 2θ range 10 °–80 ° on a Phillips ADP-3600 automated powder diffractometer equipped with a crystal monochromator employing $\text{CuK}_\alpha$ radiation.

## 3. Results and discussion

### 3.1. Gel synthesis

Tantalum pentoxide gels were synthesized under various experimental conditions employing different concentrations of $\text{Ta(OC}_2\text{H}_5)_5$:water:ethanol:HCl. $\text{C}_2\text{H}_5\text{OH}$ acts as the mutual solvent for the alkoxide and water, and HCl is the deflocculating agent. In the absence of any acid, precipitation of colloidal metal hydroxide occurred due to high reactivity of tantalum ethoxide with water, and it was not feasible to obtain clear sols. Experimental data showing the effect of the concentrations of various reactants on time of tantalum oxide gel formation at room temperature are given in Table I. For a given $\text{Ta(OC}_2\text{H}_5)_5/\text{C}_2\text{H}_5\text{OH}$ mole ratio, the time of gel formation, $t_{\text{gel}}$, increased with the amount of 50 % HCl added to the solution, reached a maximum, and then decreased with further increase in HCl concentration. For a fixed ratio of $\text{Ta(OC}_2\text{H}_5)_5$ to 50 % HCl, $t_{\text{gel}}$ increased with the $\text{C}_2\text{H}_5\text{OH}/\text{Ta(OC}_2\text{H}_5)_5$ mole ratio, probably because of the decrease in concentrations of the various reactants. All the gels were clear, transparent, and light yellow in colour. A typical transparent monolithic dry gel disc, ~ 1.25 cm diameter, is shown in Fig. 1.

Formation of a gel from metal alkoxide involves two simultaneous chemical processes, hydrolysis and polymerization, as depicted in Fig. 2 for tantalum pentaethoxide. The partial hydrolysis of $\text{Ta(OC}_2\text{H}_5)_5$ produces soluble $\text{Ta(OH)}_y\text{(OC}_2\text{H}_5)_{5-y}$ where $y$ varies from 1–4. The polymerization reaction which results in the formation of bridging oxygens, and leads to localized oxide networks, proceeds through condensation dehydration or dealcoholation reactions as illustrated in Fig. 2. The rates of the reactions are influenced by various experimental parameters such as nature of the alkoxide, concentrations of various reactants, water to alkoxide ratio, pH, temperature, etc. The solution viscosity increases with the extent of polymerization. When polymerization is extensive, a three-dimensional network is formed, and the solution converts into a gel.

### 3.2. Pyrolysis of gel

The room-temperature dried pale-yellow gel "TA" was calcined at different temperatures between 110 and 1450 °C for 1–48 h. The changes occurring on pyrolysis of the gel are summarized in Table II. On heating at 110 °C for 48 h the gel remained pale yellow. It became metallic (shiny) black on firing at 300 and 400 °C for 24 h each. The black colour might have resulted from some carbonization of the gel. When calcined at 500 °C for 24 h, the gel stayed shiny black along with the presence of some white particles. The powder resulting from this step was used in all further

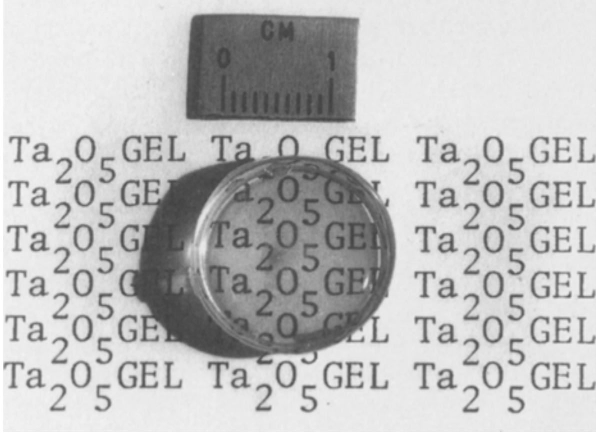

*Figure 1* Photograph showing a typical transparent monolithic ~ 1.2 cm diameter disc of dry tantalum oxide gel.

TABLE I Influence of processing conditions on time for tantalum pentoxide gel formation at room temperature

| Sample | Amounts of various chemicals used | | | Gelling time (h) |
|---|---|---|---|---|
| | $\text{Ta(OC}_2\text{H}_5)_5$ (g) | $\text{C}_2\text{H}_5\text{OH}$ (ml) | 50% HCl[a] (ml) | |
| T1 | 5 | 15 | 0.3 | 68 |
| T2 | 5 | 15 | 0.4 | 74 |
| TA | 51.8 | 150 | 5.0 | 95 |
| T3 | 5 | 15 | 0.6 | 17 |
| T4 | 5 | 15 | 0.8 | 6.5 |
| T5 | 5 | 20 | 0.6 | 35 |
| T6 | 5 | 10 | 0.6 | 2.5–3 |

[a] 50% (vol/vol) solution of concentrated hydrochloric acid in water.

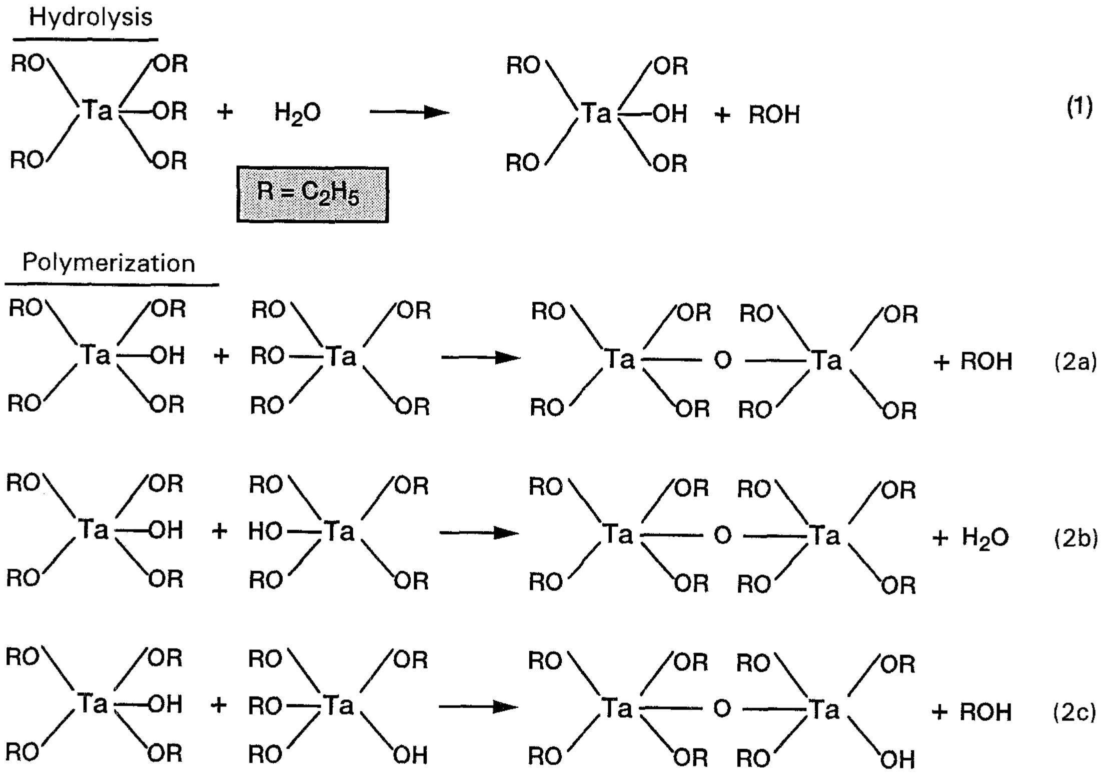

*Figure 2* Hydrolysis and polymerization reactions of tantalum alkoxide.

TABLE II Effect of various thermal treatments on tantalum pentoxide gel (TA)

| | Thermal treatment | | Phase (s) | Average crystallite size[a] (nm) | Comments |
|---|---|---|---|---|---|
| | Temp. (°C) | Time (h) | | | |
| A | Ambient | 8 weeks | Amorphous | – | Pale yellow |
| B | 110 | 48 | Amorphous | – | Pale yellow |
| C | 300 | 24 | Amorphous | – | Shiny black |
| D | 400 | 24 | Amorphous + $\beta$-$Ta_2O_5$ | ~ 30 | Shiny black |
| E | 500[b] | 24 | Amorphous + $\beta$-$Ta_2O_5$ | ~ 35.5 | Shiny black + white particles |
| F | 600 | 3 | $\beta$-$Ta_2O_5$ | ~ 40.5 | Yellowish white |
| G | 700 | 1 | $\beta$-$Ta_2O_5$ | ~ 43.5 | Light yellowish white |
| H | 900 | 1 | $\beta$-$Ta_2O_5$ | ~ 47 | As above |
| I | 1120 | 1 | $\beta$-$Ta_2O_5$ | ~ 66 | White |
| J | 1300 | 1 | $\beta$-$Ta_2O_5$ | ~ 57 | White |
| K | 1450 | 1 | $\alpha$-$Ta_2O_5$ | ~ 53 | White |

[a] Calculated from line broadening of XRD peaks.
[b] Heat treatment is cumulative up to this step; powder from this step used in all further heat treatments.

heat treatments. It turned yellowish white after heating for 3 h at 600 °C or 1 h at 700 or 900 °C. On firing at 1120, 1300, or 1450 °C for 1 h the powder remained white.

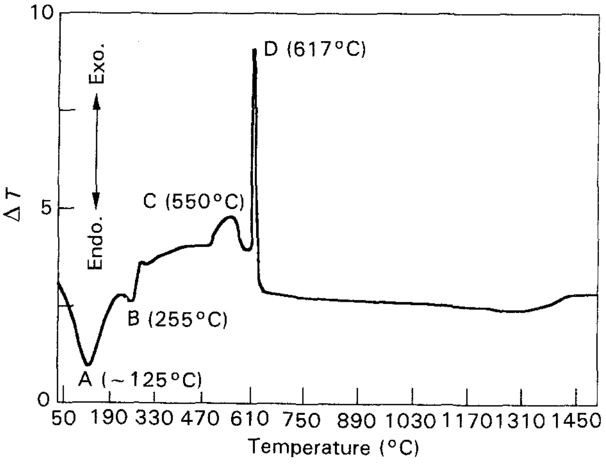

*Figure 3* A typical DTA thermogram recorded at a heating rate of 10 °C min$^{-1}$ in air for room-temperature dried tantalum pentoxide gel.

### 3.3. Thermal analyses

A typical DTA thermogram of the room-temperature dried gel "TA" recorded at a scan rate of 10 °C min$^{-1}$ in air is shown in Fig. 3. Two endothermic and two exothermic peaks are present in the DTA of the gel. The endothermic peaks A and B, with minimums at 125 and 255 °C, respectively, may be assigned to the evaporation of the residual water and alcohol present in the pores of the gel. Corresponding weight losses in the same temperature ranges are also observed in the TGA (*vide infra*). The exothermic peaks with maxima at ~ 550 and 617 °C may be ascribed to oxidation of the residual organics and the transformation of the amorphous $Ta_2O_5$ into the crystalline orthorhombic structure of $\beta$-$Ta_2O_5$, respectively. Peak C is quite broad ( ~ 480–590 °C) and probably corresponds to a process having slow kinetics. The crystallization of $Ta_2O_5$ from the amorphous gel has been reported [13] to be a nucleation and growth process. The high-temperature broad peak at ~ 1400 °C is probably due to the transformation of orthorhombic $\beta$-$Ta_2O_5$ into tetragonal $\alpha$-$Ta_2O_5$ which is in agreement with the X-ray diffraction results (*vide infra*).

A typical TGA curve of the room-temperature dried gel "TA" at a heating rate of $10\,^{\circ}C\,min^{-1}$ in air is presented in Fig. 4. It shows four distinct regions, I–IV, of weight loss. The first one occurs from room temperature to ~ 180 °C with a weight loss of ~ 8%. Region II lies between ~ 245 and 290 °C and the total loss in sample weight after this event is ~ 13%. These two processes may be attributed to the loss of residual solvents entrapped in the micropores of the gel. At the end of the third process, which occurs between ~ 518 and 605 °C, the total loss in sample weight is ~ 15%. This probably corresponds to the removal and burn off of residual organics. The reason for the sharp loss of ~ 2.2% in sample weight at ~ 684 °C, which was reproducible in three different runs, is not clear at this point. No corresponding event in this temperature range is observed in the DTA. By 1000 °C, only 81.8% of the initial sample weight is retained. In room-temperature dried gels prepared from hydrolysis of tantalum pentaethoxide (alkoxide/water = 10) in the presence of HCl (HCl/alkoxide = 0.05) or acetic acid (acetic acid/alkoxide = 13.32), Ling *et al.* [13] reported weight losses of 45% and 16%, respectively, when fired to 900 °C. This difference in weight loss is somewhat surprising particularly when compared with the results of the present study where a weight loss of only ~ 18% has been observed in the gels synthesized in the presence of HCl.

## 3.4. X-ray diffraction

Following each calcination step the gel samples were subjected to powder X-ray diffraction at room temperature for average crystal size determination and phase identification. The results are summarized in Table II. Powder XRD patterns for some of the samples are presented in Figs 5 and 6. Two broad peaks centred around 27° and 54° (2θ) are present in the gel dried under ambient conditions. On heating, these broad peaks shift to higher angles. Three broad peaks at ~ 27°, 34°, and 55° are seen in the sample calcined at 300 °C. This indicates the presence of short-range order in these amorphous materials. The sample heated at 400 °C was mostly amorphous along with the presence of some L- or $\beta$-$Ta_2O_5$ phase. On further firing at higher temperatures, the amount of the crystalline phase, $\beta$-$Ta_2O_5$, increased and the amorphous phase decreased. The material fired at 600 °C was almost fully crystalline. Many of the diffraction peaks start to split up into doublets in the powder calcined at 900 °C and have developed into independent peaks at 1120 °C. The $(1\,\underline{11}\,0)$ peak ($2\theta = 28.3°$, $d = 0.3152$ nm), $(2\,0\,0)$ peak ($2\theta = 28.8°$, $d = 0.3098$ nm, $(1\,\underline{11}\,1)$ peak ($2\theta = 36.7°$, $d = 0.2449$ nm), and the $(2\,0\,1)$ peak ($2\theta = 37.1°$, $d = 0.2423$ nm) are fully revealed at 1120 °C. The $(1\,\underline{11}\,0)$ peak has higher intensity than the $(2\,0\,0)$ peak and the $(1\,\underline{11}\,1)$ peak has more intensity than the $(2\,0\,1)$ peak. The intensities of all of the peaks increased with increasing firing temperature. Orthorhombic L- or $\beta$-$Ta_2O_5$ phase [14] is present in the samples fired up to 1300 °C, whereas the

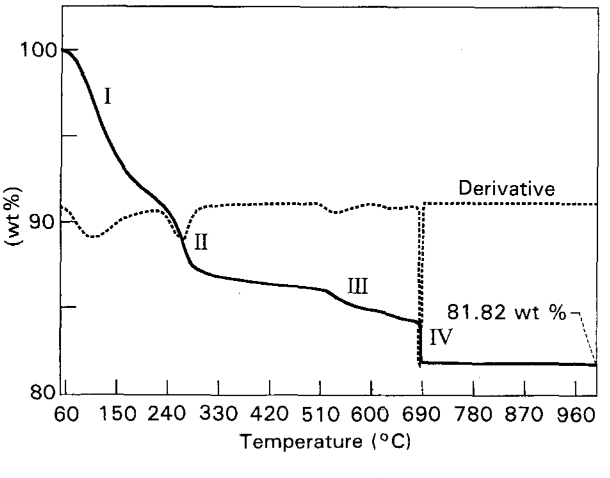

*Figure 4* A typical TGA curve recorded at a scan rate of $10\,^{\circ}C\,min^{-1}$ in air and its derivative for room-temperature dried tantalum pentoxide gel.

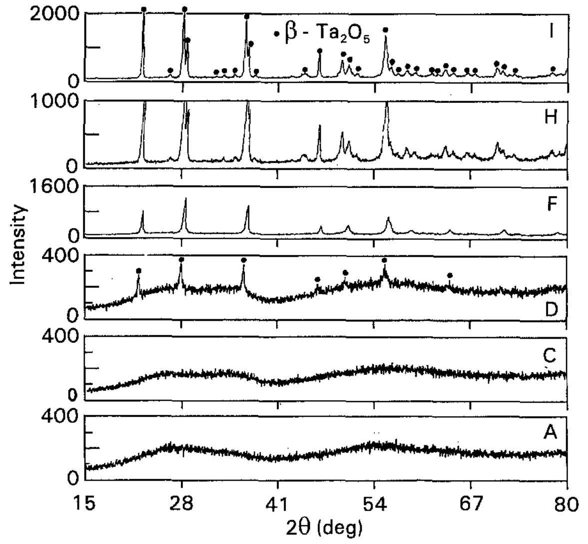

*Figure 5* Powder X-ray diffractograms of tantalum pentoxide gel specimens calcined under various conditions as shown in Table II.

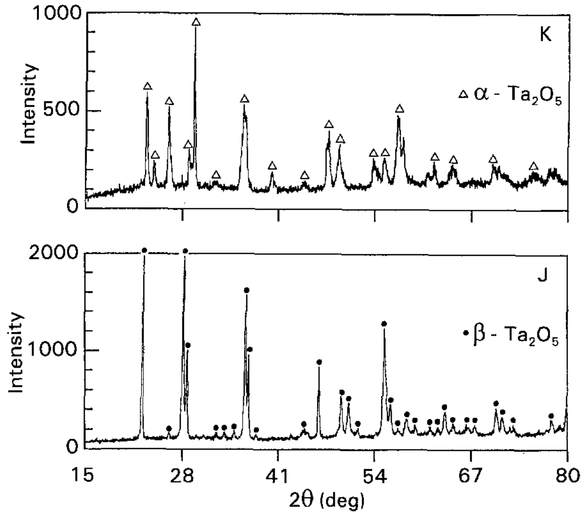

*Figure 6* Powder X-ray diffraction patterns of tantalum pentoxide gel pyrolysed to various temperatures (Table II).

phase found in the 1450 °C fired and fast-cooled specimen is tetragonal H- or $\alpha$-$Ta_2O_5$ [15]. The $\alpha$-$Ta_2O_5$ converted back into the low-temperature phase, $\beta$-$Ta_2O_5$, on slow cooling through the transition temperature of 1360 °C, indicating a slow but reversible transformation. These results are in agreement with the literature-reported [8] value of $\sim 1360 \pm 10$ °C as the transition temperature for the transformation of $\beta$-$Ta_2O_5$ into $\alpha$-$Ta_2O_5$.

After each thermal treatment the average particle size, $x$, was evaluated by X-ray line broadening analysis using the Scherrer formula

$$x = k\lambda/(B \cos\theta_B) \qquad (1)$$

where $k \sim 1$, $\lambda$ is the wavelength of $CuK_\alpha$ radiation, $B$ the width (rad) of the XRD peak at half its maximum intensity, and $\theta_B$ the Bragg diffraction angle of the line. Correction for the line broadening caused by the instrument was applied using a large particle-size silicon standard and the relationship

$$B_M^2 = B^2 + B_s^2 \qquad (2)$$

where $B_M$ and $B_s$ are the measured widths, at half-maximum intensity, of the lines from the sample and the standard, respectively. The average particle size increased with increase in calcination temperature (Table II). The X-ray line broadening technique can be utilized only for the size determination of small crystallites ($\sim 0.05$ µm). In addition, the values obtained concern not the real particle size but the average size of coherently diffracting domains, the latter being usually much smaller than the actual size of the particle.

### 3.5. Infrared spectroscopy

Infrared absorption spectra in the range 450–4000 $cm^{-1}$ were recorded for the tantalum pentoxide gel fired at various temperatures. Some typical spectra are shown in Fig. 7. Also included for comparison is the spectrum of the low-temperature orthorhombic $\beta$-$Ta_2O_5$ obtained from a commercial source. The bands in the vicinity of 1600 and 3200 $cm^{-1}$ are attributed to the absorptions due to water. The doublet at $\sim 2350$ $cm^{-1}$ is due to the atmospheric carbon dioxide. The spectra of specimens H to J, which consist of crystalline $\beta$-$Ta_2O_5$, matched exactly with that of commercial $\beta$-$Ta_2O_5$. The spectrum of sample K which had been fired at 1450 °C is different due to the formation of $\alpha$-$Ta_2O_5$ as seen from XRD.

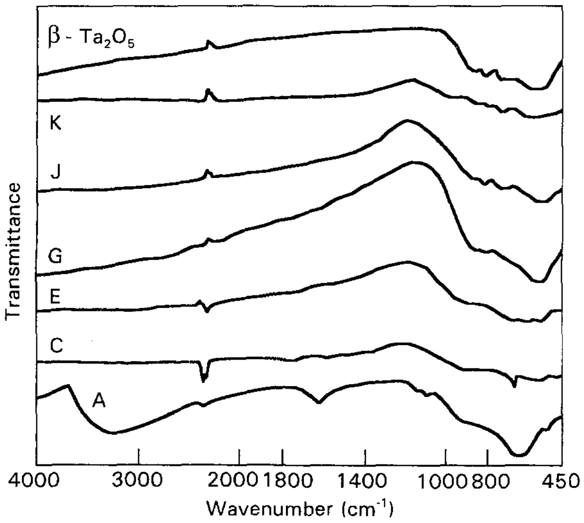

*Figure 7* Infrared absorption spectra of tantalum pentoxide gel fired under various conditions as given in Table II.

## 4. Conclusions

Tantalum pentoxide gels have been prepared as transparent monoliths and bulk powder from the hydrolysis of tantalum pentaethoxide using various experimental conditions. Ethanol was used as the mutual solvent and HCl as the deflocculating agent. Physical and structural changes occurring in the gel as a function of the calcination temperature have been monitored by DTA, TGA, X-ray diffraction, and infrared spectroscopy. The amorphous gel crystallized into the orthorhombic $\beta$-$Ta_2O_5$ on heating to $\sim 400$ °C which further transformed into tetragonal $\alpha$-$Ta_2O_5$ at $\sim 1450$ °C. The $\alpha$-$Ta_2O_5$ converted back into the low-temperature phase, $\beta$-$Ta_2O_5$, on slow cooling through the transition temperature of 1360 °C, indicating a slow, but reversible transformation. The results of this study should be useful for the application of a thin coating of tantalum pentoxide on ceramic fibres as a compliant/protective layer for the fibre–matrix interface in high-temperature composites, because of high thermal stability and excellent chemical stability of $Ta_2O_5$.

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