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Synthesis and Thermal Evolution of Structure in Alkoxide-Derived Niobium Pentoxide Gels

Narottam P. Bansal
Lewis Research Center
Cleveland, Ohio

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SYNTHESIS AND THERMAL EVOLUTION OF STRUCTURE IN ALKOXIDE-DERIVED NIOBIUM PENTOXIDE GELS

NAROTTAM P. BANSAL

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

ABSTRACT

Niobium pentoxide gels in the form of transparent monoliths and powder have been synthesized from the controlled hydrolysis and polycondensation of niobium pentaethoxide under different experimental conditions using various mole ratios of $\text{Nb}(\text{OC}_2\text{H}_5)_5:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH}:\text{HCl}$. Alcohol acted as the mutual solvent and HCl as the deflocculating agent. In the absence of HCl, precipitation of colloidal particles was encountered on the addition of any water to the alkoxide. The gels were subjected to various thermal treatments and characterized by differential thermal analysis, thermogravimetric analysis, X-ray diffraction, and infra-red spectroscopy. After drying at 400 °C, the gels were amorphous to X-rays. The amorphous powder crystallized into the low-temperature orthorhombic form of Nb_2O_5 at ~ 500 °C, which transformed irreversibly into the high-temperature monoclinic $\alpha\text{-Nb}_2\text{O}_5$ between 900 to 1000 °C. The kinetics of crystallization of the amorphous niobium pentoxide have been investigated by non-isothermal differential scanning calorimetry. The crystallization activation energy was determined to be 399 kJ/mol.

1. INTRODUCTION

The sol-gel technique has recently received significant attention¹ for the preparation of glasses, ceramic fibers, protective and other coatings, optical films, ultrapure monosized fine ceramic powders, composite materials, etc. The metal oxides synthesized by this method are generally amorphous. The structures and crystallization of these materials is of scientific interest and their stability at elevated temperatures is technologically important. Metal oxides such as niobium pentoxide may find new applications in the form of reversible cathodes^{2,3}, display devices⁴, ferroelectric ceramics⁵, and fiber coatings. However, very little attention⁶ has been paid to the synthesis of these materials by the sol-gel process. The present study was undertaken with

the objective of synthesizing the niobium pentoxide monolithic bodies and powder using the sol-gel technique. Another purpose was to investigate the thermal evolution of the physical and structural changes occurring in the gel.

Transparent monolithic niobium pentoxide gel bodies and powder were prepared under different experimental conditions. The gel was characterized by various techniques. The kinetics of crystallization of the amorphous gel powder have been studied by differential scanning calorimetry. The thermal evolution of various crystalline phases in this material was monitored by powder X-ray diffraction and the structural changes by infrared spectroscopy.

2. EXPERIMENTAL METHODS

Niobium pentaethoxide, $\text{Nb}(\text{OC}_2\text{H}_5)_5$, from Alfa products and 200 Proof absolute ethanol were used as received. The quantities of various chemicals used are shown in Table I. Due to the high reactivity of niobium pentaethoxide towards moisture, it was handled inside a glove box. Required amounts of $\text{Nb}(\text{OC}_2\text{H}_5)_5$ were mixed with alcohol and the container was sealed with parafilm and taken out of the glove box. A 50%(v/v) HCl solution (prepared by mixing equal volumes of concentrated hydrochloric acid and water) was slowly added dropwise with constant stirring. A clear homogeneous solution resulted. In some cases more water was slowly added under vigorous stirring. The container was sealed with parafilm and kept at ambient conditions for gelation. Depending upon the concentrations of different reactants, several hours to many days were required for complete gelation.

The gels were dried for several days under ambient conditions. The dried gel was fired at various temperatures between 110 to 1450 °C in air in a platinum crucible. Thermal evolution of the gel after various heat treatments was monitored by several techniques. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out 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 from 4000 to 450 cm^{-1} using the KBr pellet technique 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°/2 θ step; count time 0.5 sec) in the 2 θ range 10 to 80° on a Phillips

ADP-3600 automated powder diffractometer equipped with a crystal monochromator employing copper K_{α} radiation.

The kinetics of crystallization of the amorphous niobium pentoxide gel powder were studied by non-isothermal differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-4 system interfaced with a computer. DSC thermograms were recorded using scan rates of 1 to 40 °C/min under flowing air. Samples were contained in sealed aluminum DSC pans.

3. RESULTS AND DISCUSSION

3.1. Gel Synthesis

Niobium pentoxide gels were prepared under different experimental conditions using various mole ratios of $\text{Nb}(\text{OC}_2\text{H}_5)_5:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH}:\text{HCl}$ as shown in Table I. $\text{C}_2\text{H}_5\text{OH}$ acts as the mutual solvent and HCl as the deflocculating agent. In the absence of HCl, it was not possible to prepare clear sols. Precipitation of colloidal particles was encountered on the addition of any water to $\text{Nb}(\text{OC}_2\text{H}_5)_5$ due to high reactivity of the alkoxide toward water.

In all cases the gels were clear, transparent, and light yellow in color. A typical transparent monolithic dry gel sample ~ 1.2 cm in diameter is shown in Fig. 1. The time needed for gel formation decreased with increase in water/alkoxide mole ratio (r). A comparison of NB-5 and NB-4 (Table I) shows that, for the same value of r , gelation time decreased with higher concentration of water in the solution. The HCl concentration appears to have no influence on the gelling time, as seen from a comparison of the results for NB-1 and NB-6, but its presence in the solution is necessary to avoid the precipitation of niobium hydroxide on the addition of water.

A larger batch of gel was prepared using 50 g of $\text{Nb}(\text{OC}_2\text{H}_5)_5$, 150 ml $\text{C}_2\text{H}_5\text{OH}$, and 5.0 ml of an aqueous 50% HCl(v/v) solution. The gel was allowed to dry for five weeks under ambient conditions which resulted in yellow porous pieces. It was stored in a closed container until used for further treatment and characterization and will henceforth be referred to as "NB".

3.2. Pyrolysis of Gel

The pale yellow gel "NB" was pyrolyzed at various temperatures and the results are summarized in Table II. On drying at 110 °C for ~ 46 h, the gel became yellowish brown and

changed to shiny metallic black after heating at 300 °C for 24 h. On further treatment at 400 °C for 24 h, it turned pale yellow. Some black particles, probably carbon, were also present due to incomplete oxidation of the organics. Up to this point the material was amorphous. On further heating at 500 °C for 24 h the black particles disappeared. This powder was used for all further heat treatments. The powder turned shiny white after firing for 1 h at 700 or 800 °C. It became greyish white on heating at 900 °C for 1 h. When fired for 1 h at 1000, 1120, or 1300 °C the color of the powder stayed dirty white. The powder became brownish white after heating at 1450 °C for 1 h.

3.3. X-ray Diffraction

Following each thermal treatment, the samples were subjected to powder X-ray diffraction at room temperature for phase identification and average crystal size determination. The results are summarized in Table II and the typical XRD powder patterns are shown in Fig. 2. Samples A to D were amorphous to X-rays. Two broad halos centered around 28 and 53° (2 θ) were present in the room temperature dried gel. On heating, the position of the former broad peak shifted to lower angles whereas the latter peak was more or less unaffected. The presence of these broad peaks indicated the existence of short range order in these amorphous materials. The low-temperature orthorhombic form⁷ of Nb₂O₅ crystallized on firing at 500 °C and this phase persisted up to 900 °C (samples E to I). The amount of this crystalline phase increased with the firing temperature. The peaks at 2 θ = 28.3° and 36.5° started to split into doublets at 700 °C and had fully developed into independent peaks at 900 °C. The (180) peak (2 θ = 28.3°, d = 3.15 Å), (200) peak (2 θ = 28.9°, d = 3.09 Å), (181) peak (2 θ = 36.6°, d = 2.46 Å), and (201) peak (2 θ = 37.0°, d = 2.428 Å) were fully revealed in the 900 °C fired sample. The (180) peak has higher intensity than the (200) peak and the (181) peak was more intense than the (201) peak. The low temperature orthorhombic form transformed into the high-temperature monoclinic modification⁸, α -Nb₂O₅, on firing between 900 to 1000 °C. This was an irreversible transformation, i.e., the α -Nb₂O₅ did not convert back into the low temperature form on cooling.

The average particle size, after each heat treatment, was estimated from X-ray line broadening analysis using the Scherrer formula:

$$x = k\lambda / (B \cos \Theta_B) \quad (1)$$

where x is the average particle size, $k \sim 1$, λ the wave length of copper K_α radiation, B the width (in radian) of the XRD peak at half its maximum intensity, and Θ_B the Bragg diffraction angle of the line. Correction for the line broadening by the instrument was applied using a large particle size silicon standard and the relationship:

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

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 (Table II) with the pyrolysis temperature. The X-ray line broadening method can be used only for the size determination of small crystallites ($\sim 0.05 \mu\text{m}$). Besides, the information obtained concerns 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 particles.

3.4. Thermal Analyses

Thermal analyses of various gels were carried out after drying under ambient conditions. Typical DTA and TGA curves of the NB-2 gel recorded at a heating rate of $10^\circ\text{C}/\text{min}$ are presented in Fig. 3 and 4, respectively. Two endothermic and two exothermic peaks are present in the DTA. The TGA shows a total weight loss of 26.7% to 950°C taking place in three steps. The large endothermic peak A at $\sim 125^\circ\text{C}$ may be attributed to the loss of residual water and alcohol entrapped in micropores of the gel. The TGA shows a substantial weight loss of $\sim 18.5\%$ from room temperature to $\sim 220^\circ\text{C}$ (step I). The second endothermic peak B at 390°C in the DTA and the $\sim 6.4\%$ weight loss in the temperature region 355 to 423°C (step II) in TGA may be assigned to the loss of structural water by dehydration condensation of hydroxyl groups. The exothermic peak C at $\sim 492^\circ\text{C}$ in the DTA and the $\sim 0.5\%$ loss of weight from ~ 518 to 540°C (step III) in the TGA are probably caused by oxidation of the residual organics. The exothermic peak D at $\sim 535^\circ\text{C}$ in the DTA is ascribed to the crystallization of the amorphous material into the low-temperature orthorhombic form⁷ of Nb_2O_5 as confirmed from

XRD (*vide supra*). No thermal event corresponding to the transformation of the low temperature form of Nb₂O₅ into its high-temperature modification⁸, α -Nb₂O₅, is observed in the DTA.

3.5. Crystallization Kinetics

A variable heating rate DSC method was used to evaluate the kinetics of crystallization of the amorphous niobium pentoxide. DSC scans were run at various heating rates between 1 and 40 K/min. A typical DSC thermogram recorded at a scan rate of 10 K/min is presented in Fig. 5. A sharp exothermic peak which may be assigned to crystallization of the amorphous material into niobium pentoxide is observed at 578 °C. The peak maximum temperatures at various heating rates are listed in Table III. The position of the exotherm shifted to higher temperature with increase in scan rate.

The kinetic model of Bansal et al.⁹ was used to evaluate the values of the kinetic parameters from the DSC data. This model is expressed by the equation:

$$\ln [T_p^2/\alpha] = \ln(E/R) - \ln \nu + E/(RT_p) \quad (3)$$

where T_p is the peak maximum temperature, α the heating rate, E the activation energy, R the gas constant, and ν the frequency factor. The crystallization kinetic parameters (E and ν) are related to the reaction rate constant (k) by an Arrhenius-type expression:

$$k = \nu \exp[-E/RT] \quad (4)$$

Equation (3) is an extension of the Johnson-Mehl-Avrami¹⁰ isothermal kinetic model for use in non-isothermal methods. In the derivation of eq.(3) it was assumed that the rate of reaction is maximum at the peak which is a valid assumption for the power-compensated DSC. It has been demonstrated in earlier studies^{9,11-13} that the kinetic parameters determined from non-isothermal DSC using eq.(1) and from isothermal methods are in excellent agreement.

A plot of $\ln[T_p^2/\alpha]$ versus $1/T_p$ for the crystallization of amorphous niobium pentoxide prepared by the sol-gel technique was linear (Fig. 6) indicating the applicability of the kinetic model of Bansal et al.⁹ From linear least-squares fitting, the values of the kinetic parameters

were determined to be $E = 399 \text{ kJ mol}^{-1}$ and $\nu = 3.7 \times 10^{22} \text{ sec}^{-1}$, the correlation coefficient being 0.99.

3.6. IR Spectroscopy

Infrared absorption spectra of the niobium pentoxide gel calcined at various temperatures were recorded between 450 to 4000 cm^{-1} . Typical results are presented in Fig. 7. Also shown for comparison is the spectra of the high temperature $\alpha\text{-Nb}_2\text{O}_5$ phase obtained from a commercial source. The bands in the vicinity of 1650 and 3200 cm^{-1} are assigned to the absorptions due to water. The peak at $\sim 2280 \text{ cm}^{-1}$ is due to atmospheric carbon dioxide. As seen from XRD analysis, sample D is amorphous, F is the low temperature form, and K is the high temperature or α - modification of Nb_2O_5 . The IR spectra of these three samples are quite distinct. The spectra of sample K is quite similar to that of the commercial $\alpha\text{-Nb}_2\text{O}_5$. The peak at $\sim 835 \text{ cm}^{-1}$ may be attributed¹⁴⁻¹⁹ to the Nb-O-Nb bonding parallel to the b-axis. The Nb-O-Nb bridging bond probably causes¹⁴⁻¹⁹ the absorption band around 690 cm^{-1} and the absorption peak at $\sim 500 \text{ cm}^{-1}$ may be assigned¹⁴⁻¹⁹ to the ONb_3 structure.

It has been well established²² by NMR spectroscopy that niobium pentaethoxide forms dimers which exist as the edge-shared octahedral structure as shown in Fig. 8. In this structure, each metal atom is bonded to two bridging and four terminal groups. The bridging Nb-O band and the terminal Nb-O band appear²³ at 485 and 575 cm^{-1} , respectively, and the bridging C-O band and the terminal C-O band appear²³ at 1030 and 1066 cm^{-1} , respectively.

Not many studies have been reported on the hydrolysis of niobium alkoxides. Yamaguchi et al²⁴ synthesized a continuous series of solid solutions in the $\text{Nb}_2\text{O}_5\text{-Ta}_2\text{O}_5$ system by the simultaneous hydrolysis of niobium and tantalum isopropoxides. Alquier et al.⁶ have prepared niobium pentoxide gels using different approaches such as destabilisation of a sol obtained by controlled hydrolysis of NbCl_5 with H_2O_2 and also by hydrolysis of $\text{Nb}(\text{OC}_2\text{H}_5)_5$ and niobium chloroalkoxides. The addition of H_2O_2 seemed to improve the process by removing chloride ions from the system through a redox reaction:



On hydrolysis of niobium pentaethoxide with tetramethylammonium hydroxide in methanol, decaniobate anion $\text{Nb}_{10}\text{O}_{28}^{6-}$ is formed.²⁰ Fuchs et al.²¹ have reported the formation of various isopolyniobate ions, $\text{Nb}_6\text{O}_{19}^{6-}$, $\text{Nb}_{12}\text{O}_{37}^{14-}$, $\text{Nb}_{24}\text{O}_{65}^{10-}$ on hydrolysis of $\text{Nb}(\text{OC}_2\text{H}_5)_5$ with various organic bases at various water/Nb mole ratios. It is difficult to predict if such ionic species are present in our gels which are produced without the presence of an organic base.

Alquier et al.⁶ have carried out gelation of $\text{Nb}(\text{OC}_2\text{H}_5)_5$ using water/Nb mole ratio > 5.5 . Due to the high reactivity of $\text{Nb}(\text{OC}_2\text{H}_5)_5$ with water, it was suggested that most probably the main reaction is:



rather than



It was suggested that gelation must proceed through an ololation/oxolation process between $\text{Nb}(\text{OH})_5$ molecules with elimination of water rather than polycondensation between hydroxoethoxy niobates with elimination of ethanol. A more detailed investigation is needed to decide whether reaction (6) or (7) is predominant.

4. SUMMARY AND CONCLUSIONS

Transparent monoliths and bulk powder of niobium pentoxide gels can be prepared from the hydrolysis of niobium pentaethoxide using hydrochloric acid as the deflocculating agent. The thermal evolution of physical and structural changes occurring in the gel were monitored by DTA, TGA, X-ray diffraction, and infrared spectroscopy. The gels were amorphous to X-rays and crystallized into the low-temperature form of Nb_2O_5 at $\sim 500^\circ\text{C}$, which transformed into the high-temperature H- or α - Nb_2O_5 modification between 900 to 1000°C . This transformation was irreversible i.e. the α - Nb_2O_5 did not convert back into the low temperature form on cooling. The kinetics of crystallization of the amorphous powder were studied by non-isothermal DSC and the crystallization activation energy was evaluated to be 399 kJ/mol .

niobium pentoxide on ceramic fibers for reinforcement of the high temperature ceramic matrix composites because of the thermal and chemical stability of Nb_2O_5 .

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TABLE I. Effect of Synthesis Conditions on Gelling Time and Appearance of Niobium Pentoxide Gels

Gel #	Amounts of Various Chemicals Used				H ₂ O/Alkoxide Mole Ratio (r)	Gelling Time (h)	Gel Appearance
	Nb(OC ₂ H ₅) ₅ (g)	C ₂ H ₅ OH (ml)	50% HCl ^a (ml)	H ₂ O (ml)			
NB-6	5	15	0.4 + 0.1 Conc. HCl	-	0.71	205	Clear, transparent
NB-1	5	15	0.4	-	0.71	205	Clear, transparent
NB-5	5	15	0.6	-	1.06	40	Clear, transparent
NB-3	5	15	0.8	-	1.41	8.5	Very slightly translucent
NB-4	5	10	0.6	-	1.06	32	Clear, transparent
NB-2	5	15	0.4	0.2	1.41	0.5	Transparent; some white suspension

^a50% (v/v) solution of conc. HCl in water

TABLE II. Influence of Thermal Treatments on Niobium Pentoxide Gel (NB)

#	Heat Treatment		Phase(s)	Grain Size ^a (Å)	Comments
	Temp. (°C)	Time			
A	Ambient	5 weeks	Amorphous	-	Pale yellow
B	110	46 h	Amorphous	-	Yellowish brown
C	300	24 h	Amorphous	-	Metallic black
D	400	24 h	Amorphous	-	Pale yellow; some black particles.
E	500 ^b	24 h	Nb ₂ O ₅ ^c	355	Dark yellow when hot, pale yellow when cold.
F	600	3 h	Nb ₂ O ₅ ^c	355	Light orange when hot, pale yellow when cold.
G	700	1 h	Nb ₂ O ₅ ^c	378	Shiny white
H	800	1 h	Nb ₂ O ₅ ^c	490	Shiny white
I	900	1 h	Nb ₂ O ₅ ^c	514	Dirty white
J	1000	1 h	α-Nb ₂ O ₅	308	Dirty white
K	1120	1 h	α-Nb ₂ O ₅	355	Dark yellow when hot, dirty white when cold.
L	1300	1 h	α-Nb ₂ O ₅	470	Dark yellow when hot, dirty white when cold.
M	1450	1 h	α-Nb ₂ O ₅	693	Orange yellow when hot, brownish white when cold.

^aAverage size evaluated from line broadening of XRD peaks.

^bHeat treatment is cumulative up to this step; powder from this step used in all further heat treatments.

^cJ.C.P.D.S. Card # 27-1003

TABLE III. Effect of Heating Rate on the Peak Maximum Temperature of the DSC Exotherm for the Crystallization of Amorphous Niobium Pentoxide

Heating Rate, α (K/min)	Peak Maximum Temperature, T_p (K)	Heating Rate, α (K/min)	Peak Maximum Temperature, T_p (K)
1	818	10	852
2	828	15	853
2	832	15	860
5	838	20	860
5	841	30	868
10	851	40	871

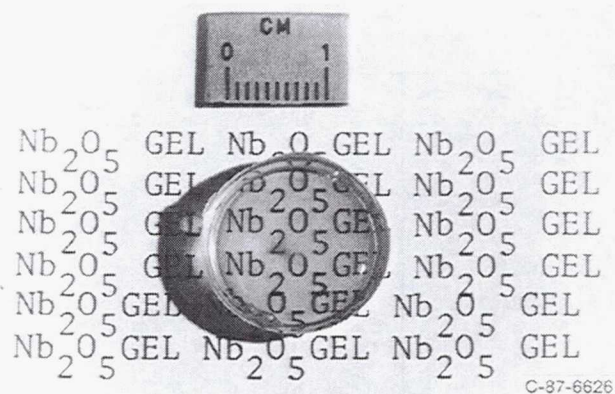


Figure 1.—A typical sample of dried niobium oxide gel.

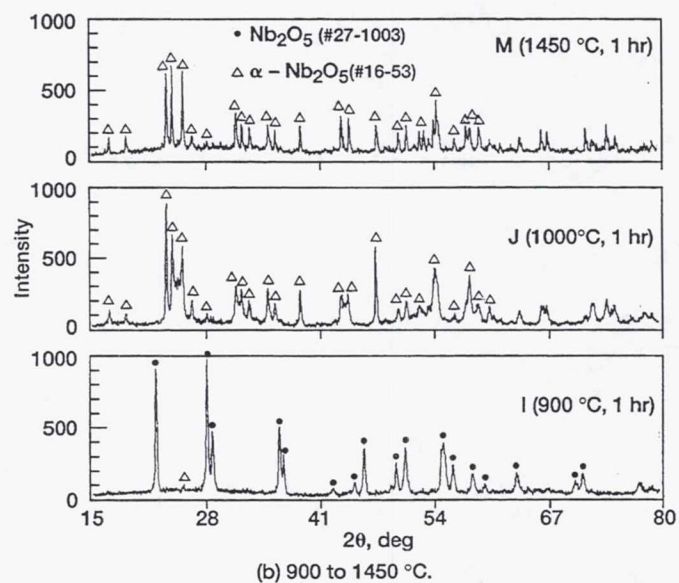
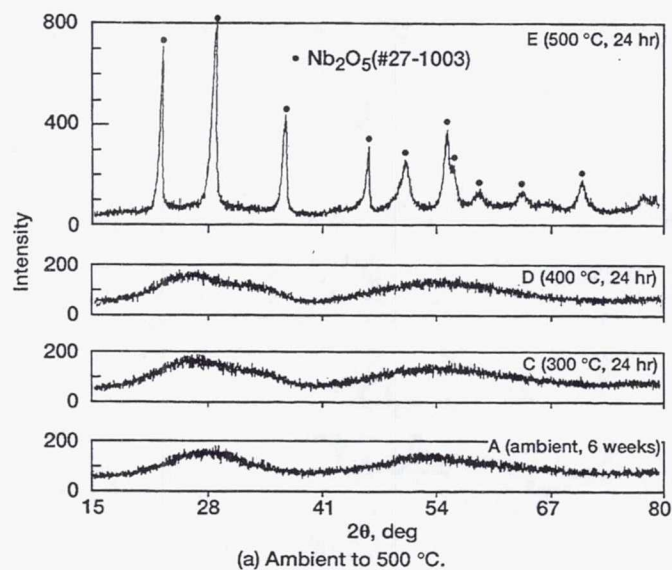


Figure 2.—Powder x-ray diffraction patterns of niobium pentoxide gel samples fired at different temperatures as shown in Table II.

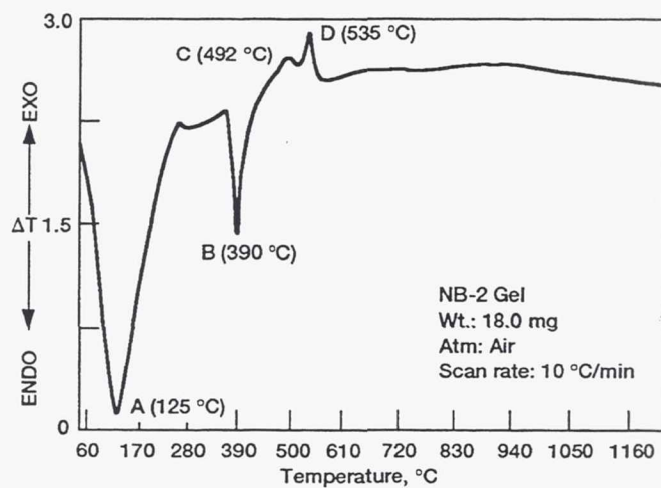


Figure 3.—A typical DTA thermogram of the niobium pentoxide gel recorded at a scan rate of 10 $^{\circ}\text{C}/\text{min}$ in air.

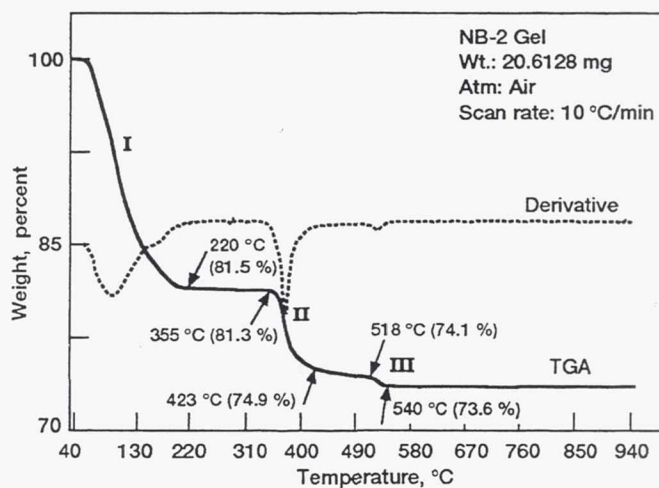


Figure 4.—TGA curve and its derivative for the niobium pentoxide gel at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in air.

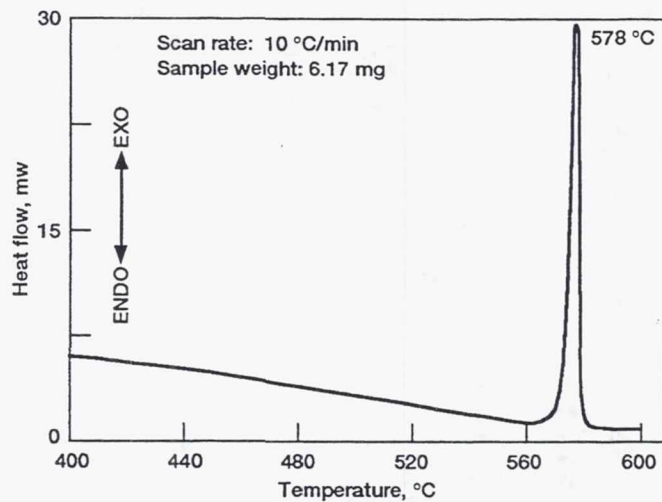


Figure 5.—A typical DSC thermogram showing the crystallization peak for the niobium pentoxide gel recorded at a heating rate of 10 °C/min in air.

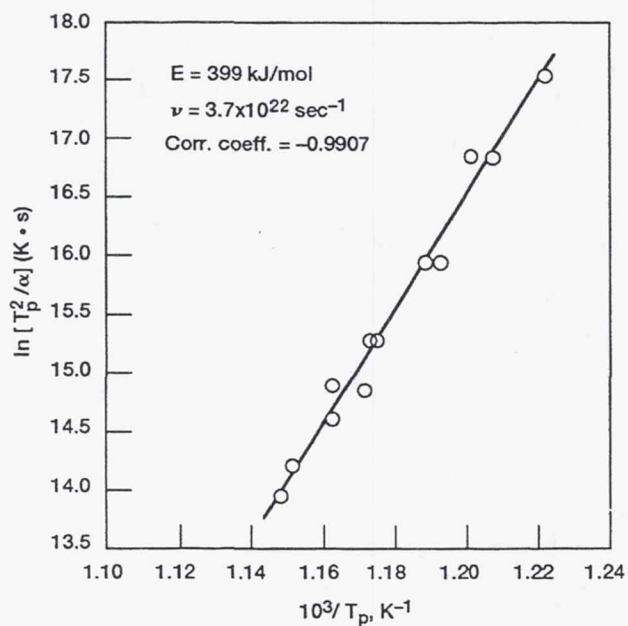


Figure 6.—Plot of $\ln[T_p^2/\alpha]$ vs. reciprocal of the DSC exothermic peak maximum temperature, T_p , for crystallization of the niobium pentoxide gel.

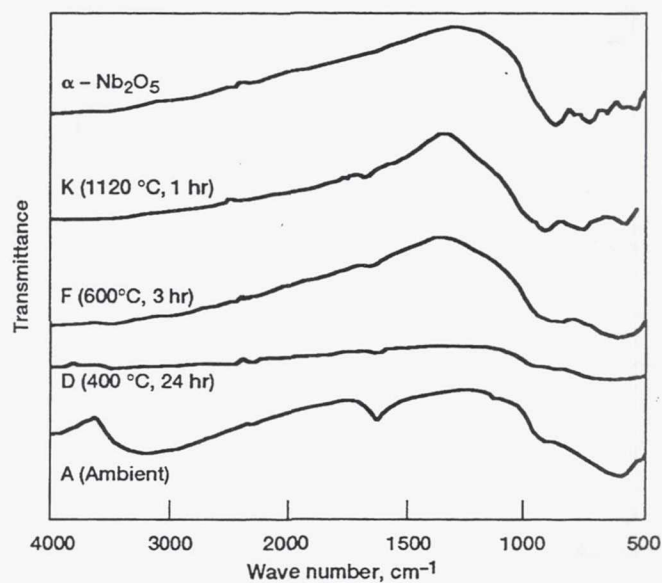


Figure 7.—Infrared absorption spectra of the niobium pentoxide gel calcined at different temperatures. For thermal histories of various samples refer to Table II.

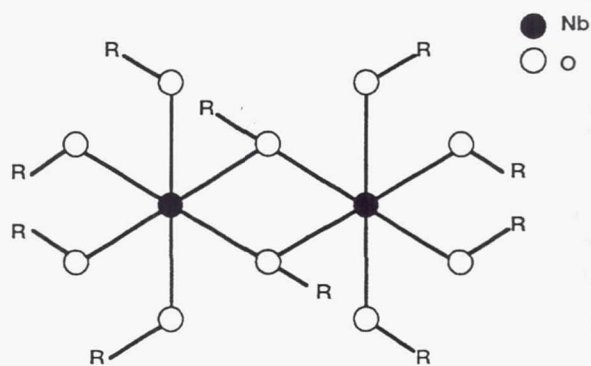


Figure 8.—The structure of niobium pentaethoxide dimer where R represents the $-\text{C}_2\text{H}_5$ group.

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13. ABSTRACT (Maximum 200 words) Niobium pentoxide gels in the form of transparent monoliths and powder have been synthesized from the controlled hydrolysis and polycondensation of niobium pentaethoxide under different experimental conditions using various mole ratios of $\text{Nb}(\text{OC}_2\text{H}_5)_5 \cdot \text{H}_2\text{O} : \text{C}_2\text{H}_5\text{OH} : \text{HCl}$. Alcohol acted as the mutual solvent and HCl as the deflocculating agent. In the absence of HCl, precipitation of colloidal particles was encountered on the addition of any water to the alkoxide. The gels were subjected to various thermal treatments and characterized by differential thermal analysis, thermogravimetric analysis, X-ray diffraction, and infra-red spectroscopy. After drying at 400 °C, the gels were amorphous to X-rays. The amorphous powder crystallized into the low-temperature orthorhombic form of Nb_2O_5 at ~500 °C, which transformed irreversibly into the high-temperature monoclinic $\alpha\text{-Nb}_2\text{O}_5$ between 900 to 1000 °C. The kinetics of crystallization of the amorphous niobium pentoxide have been investigated by non-isothermal differential scanning calorimetry. The crystallization activation energy was determined to be 399 kJ/mol.				
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National Aeronautics and
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Lewis Research Center
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