Synthesis, Decomposition and Crystallization Characteristics of Peroxo−Citrato−Niobium: An Aqueous Niobium Precursor

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The synthesis of peroxo−citrato−niobium, a novel aqueous precursor of niobium, is reported. Niobium oxalate was decomposed with acidified H_2O_2 to form a peroxo−niobium complex, which was reacted with citric acid at pH ∼ 7.5 to form the stable peroxo−citrato−niobium complex. IR and Raman spectroscopy indicate that the peroxo−citrato−niobium complex consists of tridentate bridging citrato and bidentate peroxo ligands. The aqueous complex is binuclear with peroxo groups chelated to niobium and the precipitated complex is polynuclear with bridging type peroxo groups. Due to kinetic limitations during crystallization, the formation of seven-coordinated niobium in peroxo−citrato−niobium energetically favors the formation of niobium oxides with seven-coordinated niobium, viz. TT−Nb_2O_5 and T−Nb_2O_5. Consequently, nanocrystalline metastable TT−Nb_2O_5, with a particle size of ∼25 nm, crystallizes from the peroxo−citrato−niobium complex at 580 °C. On further heating, TT−Nb_2O_5 transforms to T−Nb_2O_5 at 800 °C, M−Nb_2O_5 at 1000 °C, and H−Nb_2O_5 at 1200 °C. The nanometric particle size is retained after heating to 1200 °C and H−Nb_2O_5 has an average crystallite size of 53 nm.

Introduction

Multicomponent niobates, belonging to the perovskite and tungsten bronze crystal families, have useful electrical and electrooptic properties. Lead magnesium niobate (PMN) is one of the most important niobate ceramics with potential applications in capacitors and transducers. In general it is difficult to synthesize phase pure lead based perovskites by the conventional mixed-oxide process, due to the formation of a deleterious pyrochlore phase. Therefore, there has been much research on solution techniques for the synthesis of PMN. Several niobium precursors have been utilized for PMN processing including niobium ethoxide,[1] niobium chloride,[2] and potassium orthoniobate.[3] However, progress has been hindered by the often unacceptable characteristics of most niobium precursors. For example, the expense and moisture sensitivity of niobium alkoxides limits their general applicability. Halide compounds are undesirable as even small concentrations of residual halide in the powder affects the densification of the ceramic during sintering and significantly increases the dielectric loss. K_3NbO_4 is also unacceptable due to the precipitation of $K_4H_4Nb_6O_{19}$ at pH < 10.5 and niobium hydroxide between pH 8 and 5.

Niobium oxalate is fairly inexpensive and does not suffer from the drawbacks of halides or orthoniobates. However, it cannot be used directly in aqueous processing of multicomponent niobates as most metal ions form relatively insoluble metal oxalates. Thus, introduction of oxalate ions may result in undesirable phase separation by metal oxalate precipitation. To circumvent this problem, a process was developed to decompose the niobium oxalate with hydrogen peroxide in the presence of citric acid to form a soluble peroxo−citrato−niobium complex. Recently we reported the synthesis of magnesium niobate[4] and lead magnesium niobate[5] using peroxo−citrato−niobium. The objective of this article is to present the synthesis and molecular structure of peroxo−citrato−niobium and illustrate the controlling influence of the structure on its decomposition and oxide crystallization characteristics.

Experimental Procedure

Materials. Niobium oxalate (20 wt % Nb_2O_5, Niobium Products Co.), lead acetate (98 wt %, Alfa Chemicals), anhydrous citric acid (99%, Aldrich Chemical Co.), hydrogen peroxide (30−31 wt %, Fluka Chemie AG), ammonium hydroxide (30 wt %, J. T. Baker Co.) and nitric acid (69−71 wt %, Fischer Scientific Co.) were obtained commercially and used without purification.

Preparation of Peroxo−Citrato−Niobium. A schematic of the experimental procedure is illustrated in Figure 1. Anhydrous citric acid (2 mol/mol of niobium) was dissolved in H_2O_2 (13 mol/mol of oxalate), and the pH was adjusted to 0.7 with HNO_3. Niobium oxalate powder was added, in small batches, with rapid stirring to the solution heated at 65 °C. Niobium oxalate addition was accompanied by brisk effervescence of CO_2, and the solution turned yellow. Heating was continued for about an hour to completely decompose the oxalates after which the solution remained a transparent yellow. The pH was slowly increased from 0.7 to 7.5 with NH_4OH to ionize the citric acid and to form the peroxo−citrato−niobium complex. Ammonia addition led to rapid evolution of O_2 and NH_3, and the solution turned colorless.

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1997.

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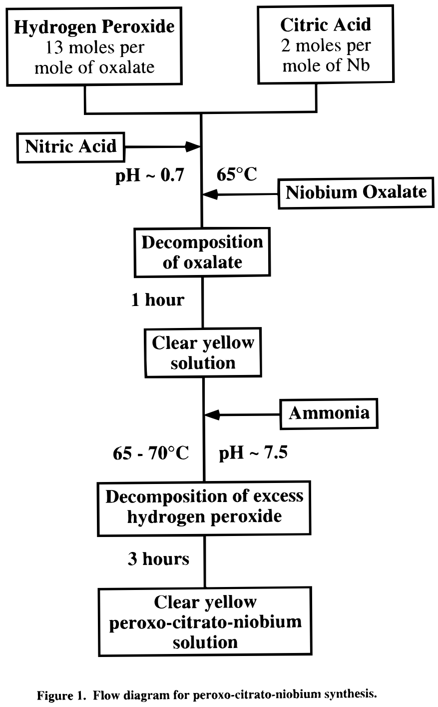

Figure 1. Flow diagram for peroxo–citrato–niobium synthesis.

After ~3 h, gas evolution ceased and the solution regained a yellow tint. Niobium concentration in the peroxo–citrato–niobium solution was 0.2 M as determined by ICP spectroscopy. The peroxo–citrato–niobium solution was stable, and no precipitation was detected even after 1 year at room temperature.

Preparation of Lead Citrate Gels. Lead acetate was added to an alkaline solution of citric acid at pH 9.5 to form lead citrate solutions with Pb:citric acid mole ratios of 1:1, 1:2, and 1:3. The lead citrate gels were prepared by evaporating water from the lead citrate solutions at 70 °C under vacuum using a rotoevaporator.

Characterization. *Niobium Oxalate.* The structure and chemical composition of the as-supplied niobium oxalate powder was determined using infrared spectroscopy, X-ray diffraction, and thermogravimetric analysis. IR spectra in the 4000–400 cm^{-1} range were recorded using KBr disks containing 0.3 wt % of the powder (FTS-60, BioRAD). TGA was performed at 1.5 °C/min in flowing air (50 cm^3/min, 951 TGA, TA Instruments). Powder crystallinity was determined by X-ray powder diffraction (Rigaku) using Cu Kα radiation.

The stoichiometry of the aqueous oxalato–niobium complexes was studied by UV spectrophotometry (8451A, Hewlett-Packard) in the 190–400 nm range using a niobium oxalate solution with a niobium concentration of 0.01 M.

Peroxo–Citrato–Niobium Solution. The ligands complexed with niobium at different stages of the synthesis process and the stoichiometry of the complexes were determined by UV spectrophotometry using a solution with a niobium concentration of 0.005 M.

The peroxo–citrato–niobium solution was concentrated from a niobium concentration of 0.2–1.5 M using a rotoevaporator (RE 51, Yamamoto). Ammonium nitrate crystallized from the solution and the crystals were separated by centrifugation. The clear supernatant was analyzed using Raman spectroscopy in a 90° scattering geometry. Raman spectra were measured with a double monochromator (Ramanor U-1000, ISA) using a cooled GaAs cathode photomultiplier detector (31034, RCA) and an argon ion laser (164, Spectra Physics). The 514.5 nm line of the laser was used at 200 mW power and a slit width of 200 mm.

Precipitate from Peroxo–Citrato–Niobium Solution. The peroxo–citrato–niobium solution was evaporated to a gel by heating it in a rotoevaporator at ~70 °C under vacuum. The peroxo–citrato–niobium complex was precipitated from the gel using an alcohol–ether mixture. The precipitate, which was extremely hygroscopic, was dried at 70 °C under vacuum and then pulverized. Attempts to grow a single crystal of the peroxo–citrato–niobium complex were not successful. Hence the structural features of the peroxo–citrato–niobium complex in the precipitate were determined using vibrational spectroscopy. The decomposition characteristics of peroxo–citrato–niobium was studied using TGA and IR spectroscopy.

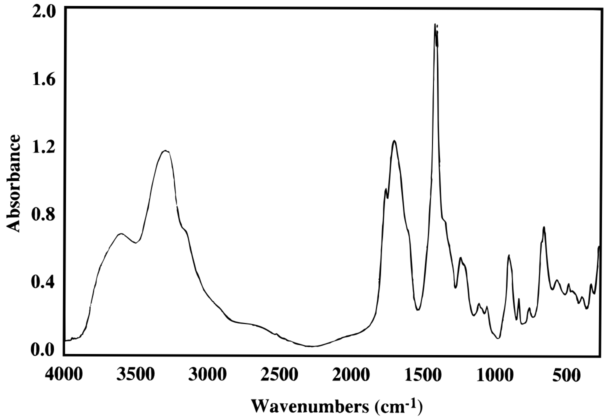

Figure 2. IR spectrum of precipitate from peroxo–citrato–niobium solution.

Discussion

Structure of the Peroxo–Citrato–Niobium Complex. In the IR spectrum of peroxo–citrato–niobium, shown in Figure 2, the carbonyl stretching frequency [ν_{as}(C=O)] of carboxyl groups complexed to niobium occurs as a strong broad band at 1670 cm^{-1}. A similar band is also observed in the spectra of malato– and tartarato–niobates.[6] Moreover, there are significant changes in the 1300–1000 cm^{-1} region in comparison to the spectra of $Na_3(C_6H_5O_7)_2$ which could indicate the coordination of the secondary hydroxyl group to niobium[7] and the presence of a planar five-membered chelate ring characteristic of α-hydroxycarboxylic acid–niobium complexes.[8] This is consistent with the observation of Dengel and Griffith[9] that only carboxylate ligands which form a five-membered chelate ring lead to ternary peroxocarboxylato complexes of Nb, Ta, W, and Mo.

Ruzdic and Brnicevic[6] observed that α-hydroxycarboxylic acid–niobium complexes such as tartarato and malato niobates are dimeric with tartarato and malato bridges, respectively. A similar dimeric structure with citrato bridges is observed in peroxo–citrato–niobium. The absorption bands at 718, 704, and 625 cm^{-1} in the IR spectra could be due to ν_1, ν_3, and ν_4 vibration modes of a metal–dioxo bridge.[10] This indicates the presence of a homodinuclear structure bridged through the deprotonated hydroxyl group of the citrate ligand, similar to dimeric citrato–Cu[11] and tetrameric citrato–Ni[12] complexes.

The strong split band at 925 and 904 cm^{-1} is assigned to the symmetric and antisymmetric stretchings of

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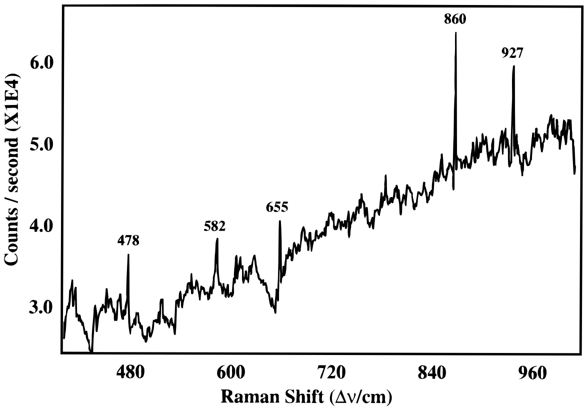

Figure 3. Raman spectrum of the peroxo–citrato–niobium solution.

terminal niobyl (Nb=O) group.[13] The intense broad bands at 3160 cm^{-1} [ν_3(N–H)] and 3028 cm^{-1} [ν_1(N–H)] are characteristic of the ammonium cation. The shoulder at 3450 cm^{-1} is attributed to the OH stretching in coordinated or physisorbed water.

In the Raman spectrum of the peroxo–citrato–niobium solution, shown in Figure 3, the characteristic ν_1(O–O) stretching of the peroxo group is observed at 860 cm^{-1}. The bands at 582 and 478 cm^{-1} can be attributed to the ν_2 (symmetric M–peroxo stretch) and ν_3 (asymmetric M–peroxo stretch), respectively.[14] The shift in the ν_1(O–O) stretching frequency from 877 cm^{-1} in H_2O_2 to 860 cm^{-1} in the peroxo–citrato–niobium complex indicates the presence of a chelated peroxo ligand. Also, the absence of additional Raman bands due to ν_1(O–O) stretching in the 880–800 cm^{-1} region may indicate the presence of a monoperoxo complex.[15]

The characteristic ν_1(O–O) stretching band of the chelated peroxo ligand is not present in the IR spectra of the precipitated peroxo–citrato–nioium complex. Transition metal–peroxo complexes, with bidentate chelating peroxo groups, possess a strong absorption band due to ν_1(O–O) stretching.[14] However, the band due to ν_1(O–O) stretching is weak or absent in peroxo complexes, such as decaamine-μ-peroxodicobalt compounds, with bidentate bridging peroxo ligands.[14] So it is possible that precipitated peroxo–citrato–niobium has bridging-type peroxo ligands in a near-centrosymmetric trans configuration, with the ν_1(O–O) stretching vibration extinct in the IR mode.

IR spectroscopy indicates that the precipitated peroxo–citrato–niobium complex consists of citrato-bridged dimeric units, linked by Nb–O–O–Nb bridges into a polynuclear complex. However, in the aqueous peroxo–citrato–niobium solution, the presence of a chelated peroxo group is observed in the Raman spectra. So it is expected that binuclear peroxo–citrato–niobium complexes with a chelated monoperoxo group are present in the peroxo–citrato–niobium solution. The peroxo bridges could be forming during the dehydration and the subsequent gelation of the peroxo–citrato–niobium solution, leading to the presence of bridging type peroxo ligands in the precipitated peroxo–citrato–niobium complex. A probable structure for the dimeric peroxo–citrato–niobium complex, present in the peroxo–citrato–niobium solution, is shown in Figure 4.

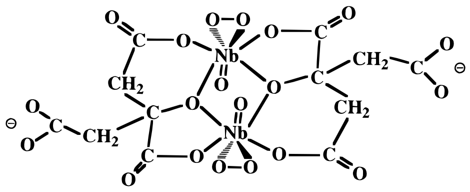

Figure 4. Structure of the dimeric peroxo–citrato–niobium complex.

As a symmetry or normal-coordinate analysis is not reported for citric acid or citrato–metal complexes the exact assignments of all the IR bands of peroxo–citrato–niobium is difficult. Also, the poor crystallinity and the structural complexity of peroxo–citrato–niobium precludes a complete theoretical analysis of its vibration spectra. Moreover the presence of adsorbed water due to the hygroscopicity of the complex leads to broad bands and limits the resolution of the different vibration bands in the 4000–3000 and 1800–1600 cm^{-1} regions of the IR spectra. So band assignments in this work are necessarily tentative but are consistent with the literature on the spectra of compounds related to the peroxo–citrato–niobium complex.

Formation of the Peroxo–Citrato–Niobate Complex. The following two stages are important for the synthesis of peroxo–citrato–niobium: (1) decomposition of oxalates from niobium oxalate to form the peroxo–niobium complex, (2) changes in the nature of the peroxo–niobium complex and decomposition of excess H_2O_2 with NH_3, and the formation of the peroxo–citrato–niobium complex. These reactions are individually discussed below:

Decomposition of Niobium Oxalate. The observed vibration spectrum of niobium oxalate powder exactly matches the spectrum of a niobium oxalate complex with an oxalate:Nb mole ratio of 1:2.[16] Additional bands characteristic of $H_2C_2O_4$[17] and ammonium ion are present in the IR spectra of the niobium oxalate powder. Very weak bands at 640 and 636 cm^{-1} corresponding to ν(Nb–O–Nb) bridges are also present, indicating the presence of minor amounts of polymeric niobium oxalates, such as $(NH_4)[Nb_2O_3(OH)_3(C_2O_4)]$.[16] The XRD pattern of niobium oxalate powder indicates a mixture of $NH_4[NbO(C_2O_4)_2(OH_2)]\cdot 4H_2O$[16] and $H_2C_2O_4\cdot 2H_2O$,[17] confirming the IR spectral assignments. The observed *d* values for the niobium oxalate complex are slightly shifted from the values reported by Muller et al.[16] due to the presence of NH_4^+ instead of Na^+ in the niobium oxalate powder. The total weight loss of the niobium oxalate powder when heated to complete decomposition is 23.2%. Accordingly it is proposed that the chemical composition of niobium oxalate powder (as supplied) is $NH_4[NbO(C_2O_4)_2(OH_2)]\cdot 4H_2O$ plus $1.46H_2C_2O_4\cdot 2H_2O$.

The oxidation of $H_2C_2O_4$ by H_2O_2 is represented by the reaction

$$H_2C_2O_4 + H_2O_2 \rightarrow 2H_2O + 2CO_2 \qquad (1)$$

Hatcher[18] observed only un-ionized $H_2C_2O_4$ molecules

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to be oxidized by H_2O_2. On the basis of the dissociation constants of oxalic acid, $H_2C_2O_4$ is the predominant species in the oxalic acid–water system when pH < 1. Therefore, H_2O_2 was acidified to pH ~ 0.7 with citric acid and HNO_3 to ensure complete oxalate decomposition. To enhance the oxidation kinetics of $H_2C_2O_4$, an excess of H_2O_2 was used (mole ratio of H_2O_2:$H_2C_2O_4$ = 13:1) and the solution was heated to 65 °C. Under these conditions, evolution of CO_2 ceased after an hour, indicating the complete decomposition of the niobium oxalate powder.

Equation 1 describes only the oxidation of excess oxalic acid in niobium oxalate but not the decomposition of the oxalato–niobium complex. An aqueous solution of niobium oxalate has an UV absorption peak at 270 nm, indicating the presence of the 2:1 oxalato–niobium complex $[Nb(OH)_2(C_2O_4)_2]^-$ [19] at pH < 1. No literature exists about the reaction between $[Nb(OH)_2(C_2O_4)_2]^-$ and H_2O_2. However, the yellow color of the solution indicates that a peroxo–niobium complex is formed[20] during niobium oxalate decomposition. Three different peroxo–niobium complexes with peroxo:Nb mole ratios of 1:1, 2:1, and 3:1 are reported in the literature.[20,21] The UV absorption characteristics of the three complexes are different with the 1:1 complex absorbing in the 255–260 nm range and the 1:2 and the 1:3 complex absorbing in the 330–380 nm range. The peroxo–niobium complex formed after niobium oxalate decomposition has a UV absorption peak at 262 nm, indicating a peroxo:Nb mole ratio of 1:1 in the complex. The small shift in the observed and reported UV absorption maxima can be attributed to bathchromic effects. On the basis of UV spectrophotometry and Muhlebach's work on peroxo–titanium complexes,[22] it is proposed that the formula for the peroxo–niobium complex is $[Nb(O_2)(OH)_2]^+$.

Niobium oxalate decomposition by hydrogen peroxide at 65 °C is then given by

$$[Nb(OH)_2(C_2O_4)_2]^- + 3H_2O_2 + 2H^+ \rightarrow [Nb(O_2)(OH)_2]^+ + 4CO_2 + 4H_2O \quad (2)$$

The observation that pH increases during niobium oxalate decomposition supports the proposed reaction mechanism.

The presence of citric acid inhibits condensation of the peroxo–niobium complex, probably due to the formation of a peroxo–citrato–niobium complex similar to the ternary EDTA– or NTA–peroxo–titanium complexes reported in the literature.[22] However, the peroxo–citrato–niobium complex formed at low pH is not very stable and undergoes a condensation reaction to form polymeric niobium complexes. A change in the UV absorption maximum to 280 nm is observed, probably due to the formation of Nb–O–Nb bridges during the condensation reaction. An amorphous precipitate forms after 3 h, and using IR spectroscopy, the precipitate was identified as peroxoniobium hydrate $HNbO_4 \cdot xH_2O$.[8,23]

Grigor'eva and Golubeva[7] also observed polymerization of the citrato–niobium complexes formed at low pH and obtained stable monomeric complexes only at pH > 5. The increase in the stability of complexes formed at high pH is attributed to the structural differences between the low pH and high pH citrato–niobium complexes. At low pH the protons of the central carboxyl and a terminal carboxyl group of citric acid are substituted by niobium leading to the formation of a seven membered chelate ring.[7] At pH > 5 the deprotonated hydroxyl and the central carboxyl groups are coordinated to niobium[7] to form a unique but stable five-membered chelate ring.[8] Therefore, to maintain niobium as a soluble species, the pH was raised to 7.5 with ammonium hydroxide to form the stable citrato–niobium complex.

Effect of Ammonia Addition. With ammonia addition, the color of the solution changed from yellow at pH ~ 1 to pale yellow at pH ~ 3 and to a colorless solution at pH > 4.5. Changes in color and in the UV absorption spectra with changing pH are also seen for peroxotitanates[22] and is attributed to changes in the composition of the complexes. Similarly, it is proposed that peroxo–niobium complexes are hydrolyzed on addition of ammonia in accordance with

$$[Nb(O_2)(OH)_2]^+ \xrightarrow{2OH^-} [NbO(O_2)(OH)_2]^- + H_2O \quad (3)$$

Ammonia addition also leads to H_2O_2 decomposition, with a strong exothermic reaction and brisk effervescence of O_2. The rapid decomposition kinetics of H_2O_2 in the presence of a base such as NH_3 and a high reaction temperature is well documented.[24] However, peroxo–niobium complexes may catalyze the reaction in a manner analogous to the catalytic effect of peroxo–Cu compounds on H_2O_2 decomposition.[25]

The decomposition of H_2O_2 is exothermic, and it is necessary to maintain the solution at 65–70 °C to prevent ebullition. However, on cooling to room temperature, a pale yellow compound precipitates from the solution. Using X-ray diffraction, the compound was identified as ammonium tetraperoxoniobate, $(NH_4)_3[Nb(O_2)_4]$.[26] The formation of this compound indicates that the monoperoxo complex $[NbO(O_2)(OH)_2]^-$ reacts with excess H_2O_2 to form $[Nb(O_2)_4]^{3-}$. $[Nb(O_2)_4]^{3-}$ is observed to decompose at temperatures >40 °C.[26] After decomposition of the excess H_2O_2, $[Nb(O_2)_4]^{3-}$ hydrolyzes with the liberation of active oxygen to form the monoperoxo–niobium complex, $[NbO(O_2)(OH)_2]^-$. The monoperoxo–niobium complex reacts with citrate ions to form the stable yellow ternary peroxo–citrato–niobium complex and its formation is given by the reaction

$$[NbO(O_2)(OH)_2]^- + C_6H_5O_7^{3-} \rightarrow [NbO(O_2)(C_6H_4O_7)]^{3-} + OH^- + H_2O \quad (4)$$

which is consistent with the observation that the pH increases from 6.8 to 7.8 with formation of the peroxo–citrato–niobium complex. The peroxo–citrato–niobium

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complex has a UV absorption maximum of 274 nm, which is different from the absorption maximum of 260 nm reported for the citrato–niobium complex.[27] The differences in the UV absorption characteristics of the peroxo–citrato–niobium complex with both peroxo–niobium and the citrato–niobium complexes confirms the formation of a ternary complex.[28] A similar shift in the absorption maximum with ternary complex formation is also observed for peroxo–tartarato–titanium and fluoro–peroxo–niobium complexes.[28]

Characteristics of the Peroxo–Citrato–Niobium Gel. On dehydrating the peroxo–citrato–niobium solution, the viscosity of the solution increases and a yellow opaque gel forms. The peroxo–citrato–niobium gel is extremely hygroscopic, very soluble in water, and insoluble in organic solvents. The gel is X-ray amorphous, except for the presence of NH_4NO_3 crystallites. The gel structure can be considered to be composed of anionic peroxo–citrato–niobium complexes and uncomplexed citrate ions linked into a three-dimensional structure. The observed breakdown of the gel structure in water and the sharp lowering of the gel viscosity with small amounts of excess water indicates the presence of ionic NH_4^+–O bridges. Cross-linking by NH_4^+–O bonds leads to polymeric structures similar to metal–citrate precipitates such as $K_2[Ni(C_6H_5O_7)(H_2O)_2]_2 \cdot 4H_2O$.[29] The amorphous nature of the gels could be due to a number of factors, including the high viscosity of the solution preventing long-range ordering, steric hindrance due to the bulky nature of the complexes, and a random three-dimensional ionic cross-linking. The peroxo–citrato–niobium complex and the excess citrate ions precipitate from the gel as ammonium compounds after alcohol–ether is mixed with the gel.

Composition of Precipitate from Peroxo–Citrato–Niobium Solution. The peroxo–citrato–niobium complex is weakly crystalline and leads to broad peaks in the X-ray diffractogram, corresponding to the *d* values 0.934, 0.846, and 0.828 nm. Apart from the peroxo–citrato–niobium complex, X-ray diffraction of the precipitate also indicates the presence of diammonium hydrogen citrate[30] and NH_4NO_3.[31] To accurately determine the chemical composition of the precipitate, ammonium nitrate was separated from the precipitate by fractional crystallization before thermogravimetric analysis. The total weight loss from the anhydrous precipitate (free of NH_4NO_3) when heated to complete decomposition was 69.7%. Accordingly, it is proposed that the chemical composition of the anhydrous precipitate is $(NH_4)_4[NbO(O_2)(C_6H_5O_7)]_2$ with $0.65(NH_4)_2(HC_6H_5O_7)$.

Decomposition Characteristics of Precipitated Peroxo–Citrato–Niobium. The TGA and DTA scans of precipitated peroxo–citrato–niobium heated in air at 1.5 and 10 °C/min are shown in Figures 5 and 6, respectively. Decomposition below 450 °C is similar for both heating rates, except for a ~30 °C shift to the higher temperature at 10 °C/min. Because of the presence of three different components in the precipitate (ammonium nitrate, diammonium hydrogen citrate, and peroxo–citrato–niobium), the decomposition behavior is complex with six or seven individual steps that can be discerned from the TGA data. The 4.3% weight loss from 25 to 100 °C can be attributed to the loss of physisorbed water and is seen as an endothermic peak in the DTA. The 31.2% loss between 100 and 250 °C is observed as a series of endothermic peaks in the DTA, indicating the onset of decarboxylation and dehydration reactions in the precursor.

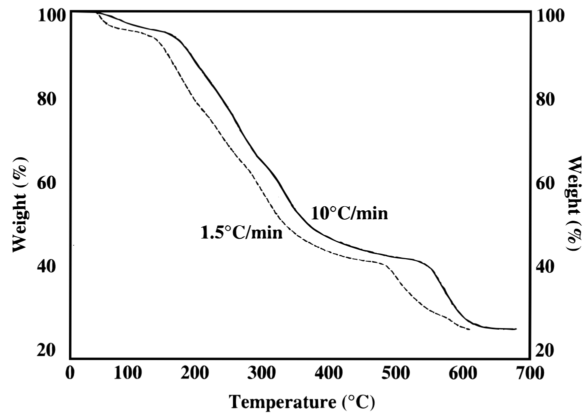

Figure 5. TGA scans of peroxo–citrato–niobium heated in air at 1.5 and 10 °C/min.

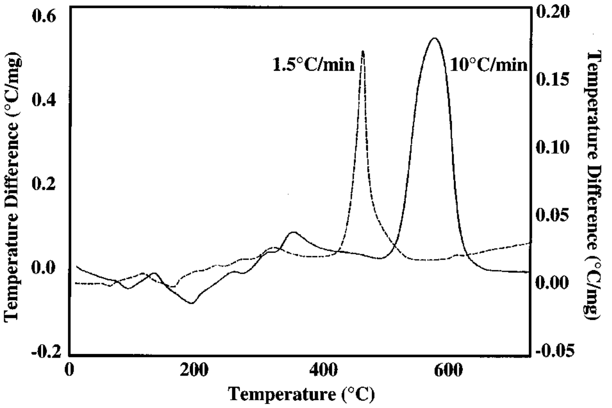

Figure 6. DTA scans of peroxo–citrato–niobium heated in air at 1.5 and 10 °C/min.

The IR spectra of the precipitate as a function of the decomposition temperature are shown in Figure 7. The bands due to ν_{as}(C=O) in the 1800–1500 cm^{-1} region and ν_s(C–O) vibrations in the 1450–1000 cm^{-1} region are unchanged after heating to 250 °C, expect for a broadening in the 1500–1750 cm^{-1} region. Also, the Nb=O band[13] at 920 cm^{-1} and bands at 710, 704, and 625 cm^{-1} corresponding to metal dioxo bridges[10] are present at 250 °C. The broad bands at 3160 [ν_3(N–H)] and 3028 cm^{-1} [ν_1(N–H)] characteristic of the ammonium cation are still present. The similarity in the IR spectra of the complex after heating to 250 °C to the as-precipitated complex indicates that the homodinuclear peroxo–citrato–niobium complex is unchanged after heating to 250 °C. Additional bands at 890 and 790 cm^{-1} due to –CH out of plane deformation of $R_1R_2C{=}CH_2$ or $R_1R_2C{=}CHR_3$ are observed at 250 °C,[32] indicating the formation of unsaturated acids such as itaconic acid or aconitic acid. Accordingly, weight loss

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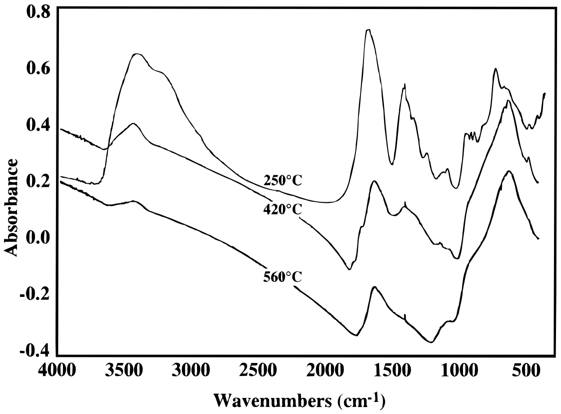

Figure 7. IR spectra of peroxo–citrato–niobium heated at 1.5 °C/min to (a) 250, (b) 420, and (c) 560 °C in air.

between 100 and 250 °C can be attributed to decarboxylation and dehydration of ammonium citrate into ammonium itaconate,[33] decomposition of nitrates,[34] and possibly the decomposition of peroxo groups in the peroxo–citrato–niobium complex.

The 38% weight loss between 250 and 450 °C occurs in two or three steps with 30% of the weight loss between 250 and 350 °C. Endothermic peaks possibly associated with dehydration and decarboxylation reactions in the peroxo–citrato–niobium complex are observed between 250 and 300 °C and a broad exothermic peak due to the oxidative decomposition of itaconic anhydride is observed at ~320 °C in the DTA. The IR spectra of the precipitate heated to 420 °C (Figure 7) is very different from the spectrum of the precipitate heated to 250 °C. The metal–oxygen vibrations between 800 and 450 cm^{-1} are observed as a broad band centered at 620 cm^{-1}, which is very similar to the [Nb–O] vibration in polynuclear complexes containing Nb–O–Nb linkages.[16,23] Bands from Nb=O vibration at 920 cm^{-1} and dioxo bridging at 710 cm^{-1} cannot be discerned in the IR spectra, indicating a change in the niobium coordination. However, the carbon–oxygen vibration region between 1800 and 1000 cm^{-1} at 420 °C is not very different from the spectrum at 250 °C, except for a broadening particularly of the C–O deformation bands in the 1200–1000 cm^{-1} region. Broadening is commonly observed during decomposition and is probably indicative of a highly strained molecular structure. The carbonyl stretching frequency [ν_{as}(C=O)] of carboxyl groups complexed to niobium occurs as a strong broad band at 1600 cm^{-1}, and the symmetric stretching is observed at 1400 cm^{-1}. The difference in the asymmetric and symmetric stretching frequency of ~200 cm^{-1} is characteristic of a bidentate bridging complex,[35] indicating that the carboxylate bridges in the niobium complex are present after decomposition at 420 °C. A shoulder at 890 cm^{-1} due to –CH of $R_1R_2C=CH_2$ and bands at 1770 and 1720 cm^{-1} due to ν_{as}(C=O) in acid anhydrides[36] are indicative of dehydration and decarboxylation reactions in the peroxo–citrato–niobium complex between 250 and 420 °C.

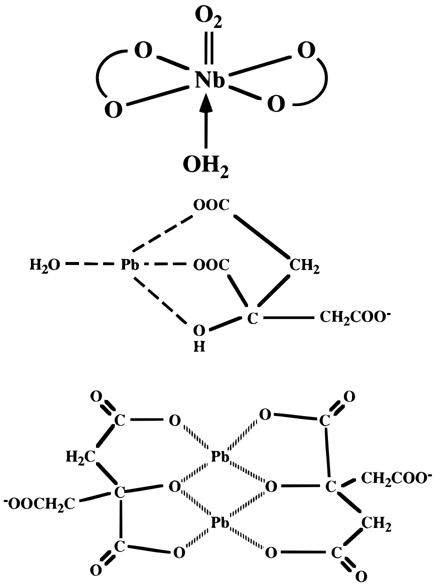

Figure 8. Structures of the (a, top) monomeric dioxalato–niobium complex $[NbO(C_2O_4)_2(OH_2)]^-$, (b, middle) monomeric citrato–lead complex $[Pb(C_6H_5O_7)]^-$, and (c, bottom) dimeric citrato–lead complex $[Pb_2(C_6H_4O_7)_2]^{4-}$.

Above 450 °C, the complex undergoes a two step decomposition when heated at 1.5 °C/min with a weight loss of 28.5% between 470 °C and 550 °C and 10.8% weight loss between 560 °C and 600 °C. Corresponding to the weight loss steps in the TGA, a broad exothermic peak is observed in the DTA between 425 and 560 °C.

The IR spectrum of the precipitate heated to 560 °C in air shows two broad bands between 1750–1500 and 800–450 cm^{-1}. The broad band centered at 1618 cm^{-1} is typical of the presence of a unidentate carboxylate ligand,[36] which indicates that the carboxylate bridges are decomposed above 470 °C. The presence of residual carboxylate ligands prevents the crystallization of Nb_2O_5 below 560 °C. Consequently, Nb_2O_5 crystallization occurs above 580 °C and is observed as a weak exothermic peak in the DTA.

Unlike the first stage of the decomposition below 450 °C, the heating rate strongly affects the decomposition characteristics of the precipitate above 470 °C. The two weight loss steps merge into a single weight loss step when heated at 10 °C/min, with a 70 °C shift in the onset temperature for decomposition from 470 to 540 °C. A large shift in the decomposition temperature with heating rate is indicative of a complex with high thermal stability and a high activation energy for decomposition.

Effect of Structure of Peroxo–Citrato–Niobium on Decomposition. The high decomposition temperature of the peroxo–citrato–niobium complex relative to other citrato–metal complexes could be related to the presence of a unique five-membered chelate ring and a dinuclear structure bridged through the deprotonated hydroxyl group of the citrate ligand. The relative importance of the citrato–metal bridges and the five-membered chelate ring on the thermal stability can be evaluated by comparing the decomposition characteristics of the peroxo–citrato–niobium with niobium oxalate which contains $NH_4[NbO(C_2O_4)_2(OH_2)]$.[16] The oxalate ligands in $NH_4[NbO(C_2O_4)_2(OH_2)]$ are also bonded to niobium through a five-membered chelate ring, but the oxalato–niobium complex is monomeric and does not contain carboxylate bridges as shown in Figure 8a.

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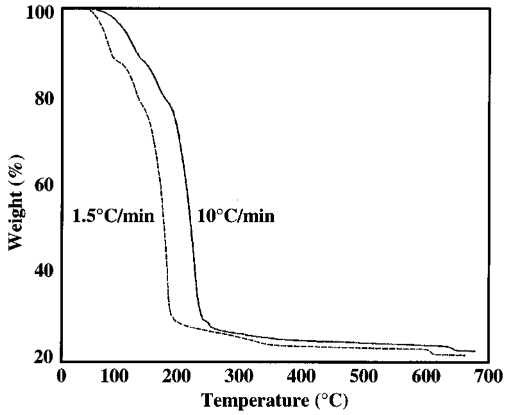

Figure 9. TGA scans of niobium oxalate heated in air at 1.5 and 10 °C/min.

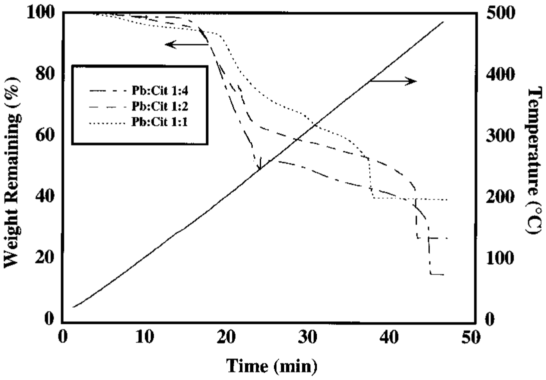

Figure 10. TGA scan of lead–citrate gels with lead:citrate mole ratios of 1:4, 1:2, and 1:1 heated at 10 °C/min in air.

The oxalato–niobium complex has a much lower thermal stability compared to the peroxo–citrato–niobium complex as observed from the TGA scans of the niobium oxalate shown in Figure 9. Niobium oxalate undergoes a three step decomposition between 25 and 300 °C. The 20.4% weight loss between 25 and 125 °C is attributed to the release of water of crystallization from the oxalato–niobium complex and $H_2C_2O_4{\cdot}2H_2O$. The 68% weight loss between 125 and 300 °C is due to the decomposition of oxalic acid and oxalato ligands in the oxalato–niobium complex. Crystallization of Nb_2O_5 is observed after a small weight loss of 4.2% at 550 °C, which could be related to the decomposition of residual carboxylate or carbonate groups in the amorphous oxide.

Structural effects on the decomposition characteristics are also observed for citrato–Pb complexes, as shown in Figure 10, similar to the carboxylato–Nb complexes. Lead citrate gels with lead-to-citrate mole ratios of 1:1 and Pb_3Cit_2 precipitates, consisting of monomeric $PbCit^-$ or $PbCit_2^{4-}$ complexes,[38] decompose at 300 °C in air. Lead citrate gels with mole ratios >1:2, consisting of dimeric $Pb_2Cit_2^{4-}$ complexes,[38] decompose at temperatures above 425 °C. Also, the decomposition temperature increases on changing the lead to citrate mole ratio in the gel from 1:2 to 1:4, concomitant with an increase in the amount of the dimeric complex in the gel. The change in the decomposition characteristics is directly related to the change in the structure of the citrato–lead complexes in the different gels. The citrate ligand is tridentate in both the monomeric and dimeric complex, with the central hydroxyl group bonded to the lead cation.[38,39] The hydroxyl group is not deprotonated in monomeric complexes, and chelation involves both terminal carboxylate ligands or the central carboxylate and a terminal carboxylate group, as shown in Figure 8b. The hydroxyl group is deprotonated in the dimeric complex (Figure 8c), leading to a homodinuclear structure bridged through the deprotonated hydroxyl group. The coordination of the citrate ligand in the dimeric citrato–lead complex is identical with the peroxo–citrato–niobium complex.

The increased thermal stability of dimeric complexes could be related to the role of the central hydroxyl group in citrate decomposition.[40] Decomposition is initiated by elimination of the hydroxyl group to form aconitic acid. Aconitates decompose into itaconates and itaconic anhydride with subsequent decarboxylation. Itaconic anhydride exothermically decomposes in air above 300 °C. Hence, deprotonation of the central hydroxyl group can expectedly alter the decomposition pathway and raise the decomposition temperature.

In the literature the effect of metal cation on the decomposition behavior of carboxylato–metal complexes is well documented.[41] However, the effect of the structure of the carboxylato–metal complex on its decomposition behavior is not well understood. The differences in the decomposition characteristics of dimeric and monomeric carboxylato–lead and –niobium complexes illustrate the ability to control the decomposition characteristics by modifying the structure of the carboxylato–metal complex.

Oxide Crystallization from Precipitated Peroxo–Citrato–Niobium. TT–Nb_2O_5 is the first crystalline phase observed after decomposition of the peroxo–citrato–niobium complex above 580 °C. From X-ray line broadening, the average crystallite size of TT–Nb_2O_5 was estimated to be ~25 nm. The specific surface area of TT–Nb_2O_5 is 40 m^2/g, which corresponds to an equivalent spherical diameter of ~30 nm, and is consistent with the crystallite size determined by X-ray line broadening. On heating, TT–Nb_2O_5 transforms to T–Nb_2O_5 at 800 °C, M–Nb_2O_5 at 1000 °C, and H–Nb_2O_5 at 1200 °C, as seen from the XRD patterns in Figure 11. The nanometric particle size is retained with increasing calcination temperature, and only a 2-fold increase in the crystallite size is observed from 25 nm for TT–Nb_2O_5 to 53 nm for H–Nb_2O_5. Consequently, peroxo–citrato–niobium has potential applications for synthesizing supported Nb_2O_5 catalysts by dip coating and thermolysis due to its capability of forming high surface area oxide films.

The structures of the different polymorphs of Nb_2O_5, except TT–Nb_2O_5, are well documented in the literature. H–Nb_2O_5, which is monoclinic, is reported to be the only stable phase at atmospheric pressure in air.[42,43] M–Nb_2O_5 is tetragonal and is considered to be a two-dimensionally ordered variant of H–Nb_2O_5.[42] T–Nb_2O_5 is a monoclinically distorted hexagonal structure and

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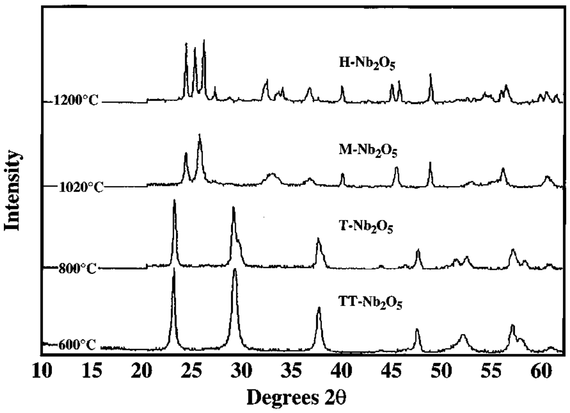

Figure 11. XRD pattern of peroxo–citrato–niobium heated to 600, 800, 1020, and 1200 °C. The polymorphs forming at the different temperatures are indicated.

is a high-pressure polymorph of Nb_2O_5 stable at pressures between 5 and 10 Kbar.[44] TT–Nb_2O_5 has a psuedohexagonal structure and is considered to be a disordered form of T–Nb_2O_5.[43–45] Weismann and Ko[43] also report that the structure of TT–Nb_2O_5 is stabilized by anion impurities such as OH, Cl, or oxygen vacancies.[43] M–Nb_2O_5 and H–Nb_2O_5 consist of only octahedrally coordinated niobium,[46] while both six- and seven-coordinated niobium atoms are present in TT–Nb_2O_5 and T–Nb_2O_5.[45]

The crystallization of TT–Nb_2O_5 and the polymorphic transformations are not unique to peroxo–citrato–niobium. TT–Nb_2O_5, with a crystallite size of ~25 nm, also crystallizes from an amorphous Nb_2O_5 containing residual carbonate or carboxylate ligands, which is formed after decomposition of the oxalato–niobium complex at 300 °C. Similarly in the literature, TT–Nb_2O_5 crystallization is also observed after dehydration of $Nb(OH)_5$ or the oxidation of Nb metal or NbO_2, with amorphous Nb_2O_5 reported as an intermediate from all three precursors.[47]

The formation of metastable polymorphs has been commonly observed in several other single-component and multicomponent systems and is usually attributed to kinetic factors such as[48] (a)topotactic dehydration of γ-AlOOH into γ-Al_2O_3[49] and (b) diffusionally limited crystallization of disordered $MgNb_2O_6$ from Mg–Nb–citrate gels[4] or the formation of extended solid solutions in systems with limited phase miscibility, such as ZrO_2–metal oxides.[50]

On the basis of the observation that TT–Nb_2O_5 and T–Nb_2O_5 contain both six- and seven-coordinated niobium similar to amorphous Nb_2O_5, Weismann et al.[43] attribute TT–Nb_2O_5 formation to diffusionally limited phenomena controlled by the coordination of niobium in the precursor. A similar kinetic effect can also explain the crystallization of TT–Nb_2O_5 from peroxo–citrato–niobium. Niobium is seven-coordinated in peroxo–citrato–niobium precipitate. Only TT–Nb_2O_5 and T–Nb_2O_5 contain seven-coordinated niobium, while M–Nb_2O_5 and H–Nb_2O_5 contain only six-coordinated niobium. Hence, the crystallization of TT–Nb_2O_5 or T–Nb_2O_5 is energetically more favorable than the M–Nb_2O_5 or H–Nb_2O_5 from the precipitated peroxo–citrato–niobium complex.

Summary

Niobium oxalate decomposes into a peroxo–niobium oxalate in excess H_2O_2 at pH < 0.7. The peroxo–niobium complex reacts with citrate ions at pH > 7.5 to form the ternary peroxo–citrato–niobium complex, $(NH_4)_4[NbO(O_2)(C_6H_5O_7)]_2$. Peroxo–citrato–niobium is dimeric with tridentate bridging and bidentate chelating peroxo ligands. Because of the formation of a five-membered chelate ring above pH 5, peroxo–citrato–niobium is stable to hydrolysis and polymerization reactions. The molecular structure of the peroxo–citrato–niobium controls its decomposition and oxide crystallization behavior.

The formation of a metal–dioxo structure in the complex also increases the decomposition temperature of the carboxylate–niobium bond in the ternary complex. Consequently, citrate bridges are stable up to 470 °C and oxide crystallization is observed above 560 °C. Metastable TT–Nb_2O_5 crystallizes from peroxo–citrato–niobium with a particle size of 25 nm. The crystallization of TT–Nb_2O_5 is dictated by topotactic effects related to the coordination state of niobium in peroxo–citrato–niobium. The formation of seven-coordinated niobium in peroxo–citrato–niobium energetically favors the crystallization of TT–Nb_2O_5, which contains niobium in both six and seven coordination, over M–Nb_2O_5 or H–Nb_2O_5, which only contain octahedral niobium. Subsequent transitions into T–Nb_2O_5, M–Nb_2O_5, and H–Nb_2O_5, the equilibrium phase, is observed on further heating. Due to its hydrolytic stability, gel formation characteristics, and ability to crystallize nanometric oxides, peroxo–citrato–niobium has potential applications for aqueous synthesis of niobate materials for ceramic and catalytic applications.

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