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KMS FUSION, INC.
P.O. BOX 1567
3621 South State Road
Ann Arbor, MI 48106

Division of Materials Sciences

RESEARCH STUDY FOR "GEL PRECURSORS AS GLASS AND CERAMIC STARTING MATERIALS FOR SPACE PROCESSING APPLICATIONS RESEARCH"

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Raymond L. Downs, PI
Wayne J. Miller, Co-I

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ABSTRACT

New opportunities to conduct containerless materials processing experiments for prolonged periods in a micro-g environment have arisen with the advent of the Space Shuttle program. This technology will presumably be expanded in the future.

This report describes the development of techniques for the preparation of glass and ceramic starting materials that will result in homogeneous glasses or ceramic products when melted and cooled in a containerless environment. Metal-organic starting materials were used to make compounds or mixtures which were then decomposed by hydrolysis and pyrolysis reactions to the corresponding oxides. The sodium tungstate system was chosen as a model for a glass with a relatively low melting temperature. The alkoxide tungstates also have interesting optical properties. For all the compositions studied, comparison samples were prepared from inorganic starting materials and submitted to the same analyses.

Attempts to form a gel from tungsten alkoxides (methoxide and isopropoxide) were unsuccessful and compromised considerably the ability to produce homogeneous metal-organic precursors for sodium tungstates. Although further work might eventually lead to a gel, our attempts, using hydrolysis at low temperatures, resulted only in precipitate formation.

Three tungsten-sodium systems were examined using 0.6, 1.0 and 2.0 molar ratios of $W(OMe)_6$ to NaOMe in methanol. These alkoxides in methanol solution gave initially homogeneous mixtures, i.e., solutions, but evaporation of the solvent produced products of unknown homogeneity. Changes in the materials during pyrolysis were monitored by optical microscopy, mass loss and chemical analysis. We observed that vapor phase hydrolysis of these products was required to prevent preferential volatilization during the pyrolysis to oxides. Most pyrolysis experiments were conducted in platinum crucibles, and resulted in crystalline products, however a small number of runs were made using a 4 meter drop tower furnace. From these experiments we isolated some clear colorless beads which when reheated slowly in a box furnace became opaque in the temperature region reported for the T_c of these compositions. A particularly noteworthy result was the formation, in low yields, of clear, glassy sodium tungstate shells from the metal-organic-derived precursor powders.

Further work with this system should be concentrated on expanded efforts to prepare gels and on more drop tower experiments. The latter should include detailed compositional analyses of individual beads or shells to unambiguously address compositional homogeneity questions from these containerless melted samples.

ACKNOWLEDGMENTS

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GEL PRECURSORS AS GLASS AND CERAMIC STARTING MATERIALS FOR SPACE PROCESSING APPLICATIONS RESEARCH

I. INTRODUCTION

I.I Gel Precursors for Containerless Processing

Containerless materials processing, which will soon be available for prolonged periods in a space environment, is an attractive route for the production of ultra-high purity glass and ceramic materials. A major advantage over conventional terrestrial processing will be the elimination of melting-container corrosion impurities. This is particularly important at high temperatures, where corrosion rates are high and the choice of crucible materials is limited. An equally promising role for containerless processing is the production of materials in an amorphous state. For example, use of crucibles in terrestrial melting of glasses can prevent formation of an amorphous state due to 1) the crystalline surface of the melt container or 2) crystal nucleation induced by crucible corrosion products. However, eliminating the melting container by space processing also means eliminating any mechanical stirring of the melt. Achieving compositional homogeneity of a space processed glass or ceramic product must therefore depend either on forced convection in the levitated melt, since natural convective forces are not available, or the use of homogeneous starting materials. If containerless processing is being conducted only to avoid container-induced crystal nucleation then it is possible to first prepare a homogeneous glass or ceramic in a terrestrial environment by conventional means (in a crucible) and then re-melt and cool the material in a containerless environment. When it is desired to eliminate crucible corrosion impurities, containerless melting of the glass or ceramic starting materials must be employed. (There may be some compositions of interest for which there is simply no compatible crucible for melting.) Without stirring of the melt, compositional homogeneity of the final product will depend largely upon the homogeneity of the starting material. The material to be melted will most likely be a compacted powder preform. The homogeneity of the starting powder is extremely important.

The use of the sol-gel route to glasses and ceramics is receiving an increasing amount of attention as a means of producing high purity compositionally homogeneous products. Recent literature reviews describe many oxide systems which have been produced from gels and the techniques employed to obtain them.[1,2]

Many of the starting materials for gel precursors can be distilled or sublimed thus yielding high purity. (It should be noted that this benefit accrues to metal-organic derived glasses and ceramics whether or not they are formed by containerless processing). However, containerless processing is a means for maintaining the purity provided by such starting materials since contaminants from the crucible are eliminated.

In principle, homogeneity of glasses from gels is possible because the gel components are combined in solution and thus mixed on a molecular scale. Maximum homogenization of the components is present at the point of gelation of the solution of glass precursor components. If this homogeneity can be maintained during gelation, drying and firing, the need for stirring of the material can be eliminated.

The use of metal-organic gels to make glass or ceramic oxides can cover a variety of techniques and starting materials. Most metal-organic derived glasses reported in the literature have been silicate based. Generally tetraethoxysilane $Si(OC_2H_5)_4$ or tetramethoxysilane $Si(OCH_3)_4$ is the silica source and principal gel former. The source of the other components used to make glasses or ceramics has depended upon the technique used by a particular investigator, the availability of the additional metal compound(s) of interest, or the compatibility of the other metal compounds with each other or the tetraethoxysilane. Compounds which have been used are: other metal alkoxides [3] e.g., $NaOCH_3$ and $Al(OC_3H_7)_3$; metal salts or organic acids, e.g., metal acetates; [4] and inorganic metal salts, e.g., nitrates.[5] Some of these same starting materials are also used to make sols (colloidal metal oxides or hydrated oxides) which can be subsequently gelled.[6] Coprecipitation of rapidly hydrolyzed metal-organic compounds has also been used to make mixed oxide precursor materials for subsequent processing.[7] The potential advantage of using all metal alkoxides, with carefully controlled hydrolysis, is the possibility of forming a three dimensional polymeric network, i.e., gel, containing all the metal compounds homogeneously dispersed and chemically bound with metal-oxygen-metal bonds. Although very homogeneous, this glass-without-melting is highly idealized since generally all the alkoxy groups will not have been removed during the hydrolysis step. These residual organic groups can be potentially disadvantageous when the gel is heated, producing unwanted carbon or excessive gas bubbles in the glass. The use of inorganic metal salts however increases the risk of compositional inhomogeneity in the gel arising from crystallization phenomena. Indeed gels are sometimes used as media for growing large uniform inorganic crystals.[8]

Gels formed by polymerization on a molecular scale are most easily accomplished with alkoxy silanes, tetraethoxysilane being the most common. This metal alkoxide can be made to hydrolyze rather slowly and the tetrahedral structure of the relatively small silicon atom can form a rigid highly crosslinked, three dimensional gel structure. As the size of the metal atom of a metal alkoxide compound increases, or the metal ion valency decreases, or the metal-oxygen bond polarity increases, the rates of hydrolysis reactions rapidly increase and the formation of a homogeneous three-dimensional gel (as opposed to a precipitate) from metal alkoxides becomes more difficult. An excellent example of this phenomenon is the preparation of silica and germania gels, both of which have been made in our laboratory and fabricated into glass shells. In both cases the starting materials were ethoxy derivatives of the metals, i.e., $Si(OC_2H_5)_4$ and $Ge(OC_2H_5)_4$. The rates of hydrolysis are vastly different; gelation of the $Si(OC_2H_5)_4$ required the use of a catalyst (0.6% H_2SO_4 was found to be particularly satisfactory at 60°C) while the $Ge(OC_2H_5)_4$ could be gelled, without precipitation, by cooling to -50°C and slowly adding a water/ethanol mixture. No catalyst was required for gelation of the germanium alkoxide.

1.2 Alkali Tungstates

Some of the most interesting oxide systems which should benefit from containerless processing are non-silicates. As an example, the production of optical glasses is particularly important. Some of the properties being sought, and the rationale for their study in space, have been described by Happe.[9]

We have chosen sodium tungstates for study since they meet the criteria of potentially benefiting from containerless processing and also extend the use of metal-organic precursors to a non-silicate oxide system having a relatively low liquidus.

Films of WO_3 can be converted, reversibly, to a dark blue color by the application of an appropriate electric field.[10] This simply achieved, but complex, physical/chemical electrochromic phenomenon has attracted attention from both an applications view, toward construction of useful electro-optical devices[11,12] and also from an academic interest in the detailed microstructure of the active color centers which are being formed.[13] The fact that electrochromic behavior is found only in the amorphous or polycrystalline state of WO_3 has lead to investigations of alkali tungstates and particularly to attempts to prepare these tungstates as glasses.[14,15]

This report describes our efforts to prepare gel precursors for sodium tungstates, observations and analytical data on the thermal decomposition and crucible melting studies of sodium-tungsten alkoxide products, and drop-tower melting experiments. Comparisons have been made with sodium tungstate products having identical composition, but prepared in a conventional manner from WO_3 and Na_2CO_3.

2. Experimental Procedure

2.1 Preparation of Metal Alkoxides

2.1.1 Preparation of $W(OMe)_6$, W(VI)

The procedure of Handy[16] et al. has been followed. The compound is prepared in two steps.

$$WCl_6 + 4\ Me_3SiOMe \longrightarrow (MeO)_4WCl_2 + Me_3\ SiCl \quad (Me=CH_3) \qquad (1)$$

$$(MeO)_4\ WCl_2 + 2\ NaOMe \longrightarrow W(OMe)_6 + 2\ NaCl \qquad (2)$$

All procedures were done either in a dry, argon-purged glove box, with continuous argon purging, or under vacuum. Tungsten hexachloride (0.19 mole) was cooled to -195°C using liquid nitrogen. Trimethylmethoxysilane (0.979 mole) was slowly added dropwise, freezing on top of the WCl_6. An excess of Me_3SiOMe was employed in the reaction. The temperature was gradually increased to -6°C at which point bubbles appeared in the brownish red mixture and then disappeared. The mixture was warmed to room temperature and ultimately heated to reflux for about one hour before gradually cooling to room temperature. The excess Me_3SiOMe and Me_3SiCl by-products were pumped away (< 0°C) leaving a brown powder which was sublimed at 60°C and about 10^{-4} Torr to give a yellow crystalline product, consistent with that reported by Handy et al. for $(MeO)_4WCl_2$. Calculated for $(MeO)_4WCl_2$ (weight percent); W, 48.54; Cl, 18. 71.

Found: W, 44.72 ± 0.45; Cl, 18.68. This product was dissolved in methanol to give a 0.48 M solution. A slight excess of NaOMe solution (1 M in methanol) was added such that $\frac{Na}{W} = 2.4$. A gray-blue precipitate was produced. The solubility of NaCl in methanol prevented a simple filtration to remove the soluble $W(OMe)_6$ product from the NaCl. The methanol was removed from the solution by distillation under argon and an attempt was made to extract $W(OMe)_6$, with pentane, from the resulting solid mixture. Although Bradley et al.[17] had reported significant solubility of $W(OMe)_6$ in pentane we obtained only a small amount of the alkoxide in the pentane phase which made this extraction technique impractical. The product was finally purified by sublimation, a technique used by Handy et al.[16] A white sublimate was slowly obtained at about 95°C and 10^{-4} Torr. Calculated for $W(OMe)_6$; W, 49.7. Found: W, 47.65 ± 0.80.

2.1.2 Preparation of $(i\text{-PrO})_x\ W(OMe_2)_{6-x}$

An alcohol exchange reaction was used:

$$W(OMe)_6 + x\ i\text{-Pr OH} \longrightarrow (i\text{-PrO})_x W(OMe)_{6-x} + MeOH \qquad (i\text{-Pr} = i\text{-}C_3H_7)$$

The reaction was performed in a toluene/isopropanol solution to take advantage of the azeotrope formed, enabling more complete methanol removal:

Species	B.P.(°C)
MeOH	64.5
i-PrOH	82.5
31% Toluene + MeOH	63.8
31% Toluene + i-PrOH	80.6

A clear solution of $W(OMe)_6$, toluene and isopropanol was made with the molar ratios 1:42:159 respectively. Solvent was slowly distilled off at 80.5°C. The displacement reaction was apparently slow and/or the amount of methanol produced was so small that a methanol/toluene azeotrope was not observed. Additional isopropanol was added as the remaining solvent decreased. Upon cooling to room temperature a considerable amount of white precipitate formed. This could be redissolved upon heating. (Note that $W(OMe)_6$ was much more soluble in isopropanol).

No attempt was made to positively identify the product(s). Bradley et al.[17] report $W(O\text{-}i\text{-}Pr)_6$ to be a pale yellow-green solid. Since our material appeared to be white, a likely candidate is $(i\text{-PrO})_x\ W(OMe)_{6-x}$, i.e., a partially exchanged material.

2.1.3 Preparation of $NaW(OEt)_6$

Reagan and Brubaker[18] have reported procedures for the preparation of $MW(OEt)_6$ where M is Na or K. These workers used WCl_5 as their tungsten source. However, since WBr_5 is the only tungsten (V) halogen compound commercially available, we have used it in our synthesis scheme instead of the chloride.

$$WBr_5 + 6\ NaOEt \longrightarrow NaW(OEt)_6 + 5\ NaBr \qquad (Et = C_2H_5) \qquad (4)$$

Tungsten pentabromide (0.018 mole) was cooled with liquid nitrogen. Ethanol (0.21 mole) was added slowly, freezing on top of the WBr_5. After adding all the alcohol the temperature was increased to -7°C where a green mixture was observed. Sodium ethoxide (0.10 mole, 1.96M in ethanol) was added slowly. A dark blue, almost black solution formed during the ethoxide addition but turned green when the addition was complete. The temperature was slowly raised to 25°C forming an orange solution with a white precipitate. The solvent was pumped away leaving a residue which was combined with benzene and filtered. The benzene was then pumped away leaving a yellow product presumably $NaW(OEt)_6$. Calculated for $NaW(OEt)_6$ (weight percent): Na, 5.3; W, 42.5. Found: Na, 5.94; W, 42.18.

2.1.4 Preparations of NaOMe + $xW(OMe)_6$ Products

Powders were prepared from the methoxides with $\frac{W}{Na}$ molar ratios of 0.6, 1.0 and 2.0. Tungsten hexamethoxide was combined with the requisite amount of 0.1 M sodium methoxide (in methanol) and methanol to provide a concentration of about 25 g alkoxides per liter. The clear solutions were refluxed. Upon cooling, some white precipitate was present. A precipitate was also present during reflux for the $\frac{W}{Na} = 1.0$ preparation. The solvent was stripped away under vacuum, leaving a white powder product.

2.2 Inorganic Melts

Inorganic melts were prepared from tungsten oxide powder (Cerac, certified at 99.9% purity) and anhydrous sodium carbonate (Fisher, certified ACS alkalimetric standard, assay $Na_2CO_3 = 100.0\%$). The powders were dried at 110-140°C, and weighed into platinum crucibles. The quantities used were sufficient to produce ~1 g of the final oxide composition. After weighing, the powders were mixed with a spatula and then heated in a box furnace (Lindberg Type 51441 with temperature controller Type 59344). The temperature required to melt the sample varied with the WO_3/Na_2CO_3 ratio. The 55:45 samples required 700°C. Above 700°C some sublimation occurred. The 67:33 samples required 950°C. The 80:20 samples were difficult to prepare. When heated rapidly to 950°C complete melting did not occur, both liquid and solid phases were observed. When heated in 100° steps to 1200°C a mixture of discrete crystals were observed upon cooling. Some crystals were clear and colorless while others were dark green or black. Mass measurements at 100° intervals showed volatilization above 1000°C, probably preferential loss of tungsten oxide. A two phase mixture was still present, but the particles were small enough and sufficiently mixed that a small sample taken for elemental analysis was representative of the total sample. The mass loss of samples heated in stages to 950°C was very close to that calculated by assuming all the mass loss was due to decomposition of Na_2CO_3.

2.3 Hydrolysis of Alkoxide Products

The alkoxides were hydrolyzed by water in the liquid and vapor states.

2.3.1 Gelation Reactions

The pure tungsten alkoxide or mixture with sodium alkoxide was combined with alcohol to form a 0.1 to 0.2 M solution. If a clear solution resulted its temperature was decreased to about -20°C. An aqueous alcohol solution was added drop by drop to the rapidly stirred alkoxide. After adding the desired amount of water the solution was allowed to slowly warm to room temperature.

2.3.2 Vapor Phase Hydrolysis of NaO Me · W (OMe)$_6$ Mixtures

The alkoxides were exposed to 80% R. H. at 300°C for 1 to 3.5 hrs in a humidity chamber (Blue M VP-100 AT-1). The mass of the alkoxide products was determined before and after exposure to water vapor.

2.3.3 Autoclave Treatments

Autoclaving was performed on $NaW(OEt)_6$. The sample was put into an autoclave (Electric Steroclave No 25X, Wisconsin Aluminum Foundry Co.) at approximately 15 psi for one hour. A yellowish solution resulted. After a few days exposure to the labortory ambience the solvent evaporated leaving yellow crystals. Sample masses were determined before autoclaving, after removal from the autoclave and after drying at room temperature.

2.4 Pyrolysis Techniques

2.4.1 Crucible Melts

The samples were placed on pyrex dishes or platinum crucibles and heated in a box furnace. The samples were taken to the final temperature in steps, usually at 100° intervals. The samples were held at each temperature step for at least one hour. Mass changes were determined at each stage. The appearance of the samples was noted by optical microscopy and recorded by photomicrographs.

2.4.2 Drop Tower Experiments

Samples were pressed into pellets at 11 metric tons for five minutes. The pellets were broken into small pieces with a spatula. The pieces were dropped down a twelve foot vertical heated tube and collected on an aluminum plate cooled with ice water. The 7.6cm diameter alumina process tube is heated by a custom-built Keith furnace (KTRM-3.50 (6-24) 3100).

2.5 Compositional Analysis

2.5.1 Atomic Absorption Analyses

Atomic absorbtion elemental analyses were performed on many of our materials to establish purity and to help understand the processes which occurred during the various heat treatments. The analyses were not straightforward. Indeed, a great deal of effort was spent to determine the best and most accurate analytical procedures.

Two decomposition methods were used for the atomic absorption analysis of tungsten-sodium materials formed upon cooling from the melt. The materials differed substantially in physical appearance and crystalline structure depending on their preparation history.

One to two hundred milligrams of sample were weighed into a stoppered flask. The unhydrolyzed metal-organic materials were loaded into sample flasks in an argon purged glove box. Two millimeters of water were added, followed by three to five drops of concentrated NH_4OH and H_2O_2. These reagents were added successively at five minute intervals until the sample was fully decomposed. (If reagents were added in larger quantities, heat from the reaction caused the solution to boil and the sample to overflow the flask). The samples were diluted in volumetric flasks and an initial analysis was performed the same day. Both tungsten and sodium were quantified against a series of Na_2WO_4 primary standards purchased as solutions of certified concentration.

A second decomposition method was studied for the series of samples where W/Na was 2.0. These samples were generally ore-like (shiny) in appearance and were very difficult to crush. This second method was never satisfactorily developed into a reproducible method. Some samples were analyzed by this method because none other was available. Where possible, reported values were selected from individual analytical runs where secondary standards showed the most accurate results. Sample preparation began with one to two milligrams of unknown mixed with four to ten times this quantity of K_2CO_3. Fusion was performed at temperatures ranging from 800°C to 1100°C for 1 - 3 hours.

2.5.2 EDXS

Elemental analyses for tungsten and sodium were also determined by EDXS at 7000X magnification. The purpose of these measurements was to detect compositional inhomogeneities from particle to particle. The technique is very sensitive to geometric differences. Since the particles were highly irregular in shape, only very gross differences could be detected. A Kevex System 7000 unit was used.

2.6 Microscopy

Microscopy was done both optically and with SEM. A Vickers photoplan M41 and a Bausch & Lomb Stereopzoom 7 were used for optical microscopy. For SEM work, a Coates & Welter CWIKSCAN 100-4 was used.

3. Results and Discussion

This work was motivated by the desire to determine if the use of metal-organic precursors would have any advantages over conventional starting materials, for the preparation of homogeneous alkali-tungstates by containerless melting. We sought to discover; 1) what problems, if any, would arise from the presence of the organic moieties during conversion to the oxide, and 2) what techniques could be used to remove, or reduce the concentration of, the organic groups after mixing of the metal alkoxides, before firing to the oxide. A third objective was to determine if the use of metal-organic precursors would permit the formation of an amorphous or glassy state of the tungstates at temperatures below the liquidus.

We have restricted our study to the sodium tungsten system, but have examined three compositions within this system. The particular metal-organic compounds employed were metal alkoxides; ethoxides and methoxides. Several approaches were taken to convert mixtures of these metal alkoxides to corresponding sodium tungstates, preferably in the form of glasses. The first approach was to determine if a mixture of the alkoxides would spontaneously decompose to a glass by simply heating in air. This approach seemed reasonable since $NaW(OEt)_6$ was reported to spontaneously decompose at room temperature.[18] However, we found that simple pyrolysis in air could not remove all the organic groups at a temperature below the crystallization temperature of the oxide mixture.

The second approach was to remove or at least decrease the amount of organic groups in the mixture before pyrolyzing. This was accomplished by hydrolysis with gaseous water. The organic groups present are alkoxides which can be removed by the following reaction

$$M\text{-}OR + H_2O \qquad MOH + ROH \qquad (5)$$

The alcohols which are produced, methanol or ethanol in our case, are quite volatile and readily evaporate. Even this approach did not result in a glass when the hydrolyzed material was subsequently pyrolyzed.

In the third approach we attempted to remove or at least decrease the amount of organic groups before pyrolysis by hydrolyzing with liquid water. The objective here was to form a gel. In order to synthesize a gel from a mixture of metal-organic constituents, at least one of the components must be capable of forming a -M-O-M-O-M polymer chain. Thus the key to this approach was to determine if our tungsten alkoxide starting compounds could be made to form a polymer chain by hydrolysis. Unfortunately, we were not successful in preparing a gel.

The fourth and final method for preparing a sodium tungstate glass from the metal-organic precursors was to rapidly heat and rapidly quench the metal alkoxides mixtures without letting the product come in contact with a container. These experiments utilized a drop tower furnace. Only by this approach were we able to prepare any glasses.

We studied the same sodium tungstate compositional range over which Tatsumisago et al.[14,15] had been successful in preparing glassy materials by a rapid quench technique. The approximate midpoint and lower and upper points on the glassy composition range were selected.

3.1 Crucible Melts

3.1.1 Pyrolysis of Unhydrolyzed Metal Organic Precursors

To convert the alkoxide compounds directly to glass, pyrolytic decomposition must occur readily. The decomposition mechanism must also liberate carbon in the form of a volatile compound to avoid its incorportion in the molten glass. This is particularly important for systems like the tungstates which have a low liquidus temperature. Such a mechanism did not occur for our materials. When pyrolyzed at 200°C the alkoxide mixtures all turned brown or gray due to residual carbon. As the temperature was increased, carbon slowly disappeared and by 600°C the materials were mainly white. Melting occurred near 700°C. Upon cooling, the melt produced a crystalline product. In each case some sublimate was found after 200°C pyrolysis.

The amount of sublimate was qualitatively more when W/Na was not equal to one. The sublimate turned yellow at 400-500°C. The yellow color was very close to the color of pure WO_3 powder. Thus we infer that the sublimate was highly enriched in tungsten. After pyrolysis at 200°C to 500°C some "glassiness" was apparent in the materials. Generally this was manifested as an increase in reflectivity for part of the sample. However the W/Na = 2 material actually formed transparent film-like pieces that appeared to have peeled away from the top surface. An example is shown in Figure 1. The film-like pieces are likely to be tungsten poor since a fair amount of sublimation occurred in this sample at low temperature.

A description of the physical changes which occur at 100° intervals, as noted by optical microscopy, is given in the appendix in Tables A-1 through A-4. One can conclude from these observations that glass formation has not occurred below the liquidus and the products that are produced upon cooling from the melt are probably crystalline.

Inorganic WO_3/Na_2CO_3 powder mixtures were pyrolyzed at 100° intervals for comparison with the metal-organic derived materials. Details of their thermal response are provided in Tables A-5 and A-6 of the Appendix for the W/Na=0.6 and W/Na=2 powder mixtures.

3.1.2 Pyrolysis of Hydrolyzed Metal-Organic Precursors

In order to remove the alkoxide groups the materials were hydrolyzed with water vapor. The hydrolysis was accomplished by either the mild condition of exposure to humid air at room temperature or the severe condition of pressurized steam in an autoclave.

Hydrolysis by exposure to humid air did not remove all the residual carbon, as evidenced in all cases by the light brown or gray color observed after pyrolysis. However, the discoloration due to carbon was much less than that seen for the unhydrolyzed material.

All samples, except for the W/Na = 2 sample, turned light gray or white at 400°C - 600°C, and formed a crystalline product upon cooling from the melt at about 700°C. The W/Na = 2 sample formed a mixture of yellow particles and dark particles with some melted particles as the temperature was raised from 200°C to 500°C. This indicated gross inhomogeneity. A very dark green melt occurred near 900°C. Further details on each mateiral are given in Tables A-7 to A-10 in the Appendix.

Only $NaW(OEt)_6$ was hydrolyzed under the more severe conditions of pressurized steam. A yellow liquid with dark yellow particles resulted. Yellow crystals formed after drying at room temperature. Pyrolyzing the crystals at 550°C produced white material with black spots. The material became all white at 650°C. At 700°C the material melted and when cooled gave a white crystalline solid. As in the case of the unhydrolyzed samples, from the physical appearance of all the samples there is no suggestion of glass formation before melting and the product(s) formed upon cooling from the melt appears very crystalline. Decomposition does not occur at a sufficiently low temperature to make possible a glassy product.

3.1.3 Thermal Analysis

The mass losses that occur during pyrolysis can aid in interpreting some of the physical and chemical changes in the materials. They can give an indication of final stoichiometry as well as signal any abnormal behavior during pyrolysis. The mass losses observed at 25°C, 200°C and 700°C are presented in a bar chart format in Figure 2. Table 2 shows the final mass losses observed for the pyrolyzed materials and for two of the WO_3/Na_2CO_3 mixtures. The expected mass losses given in Table 2 assume sodium and tungsten are completely converted to Na_2O and WO_3.

Considering for the moment only the hydrolyzed alkoxides, the actual mass losses observed agree well with the expected losses, although for the NaOMe and $0.6W(OMe)_6$ mixture a somewhat better agreement would occur if the product had a single methanol of solvation. This would have resulted in a total expected mass loss of 39.8%. The unhydrolyzed metal-organic products with W/Na = 0.6 and W/Na = 2.0 gave higher mass losses than expected for conversion to oxides. This is consistent with the sublimation observed during the pyrolysis of these materials (see Tables A-I and A-3 of the appendix). The sublimates seemed to be tungsten enriched, a not unexpected result since $W(OMe)_6$ can be sublimed, in vacuum, at 60°C. For the unhydrolyzed mixture there may be little bending between the sodium and tungsten compounds which would inhibit evaporation of $W(OMe)_6$. (See however the following discussion).

The W/Na = 1 products, from both NaOMe +$W(OMe)_6$ (VI) and $NaW(OEt)_6$(V), gave mass losses upon pyrolysis which are much closer to that for theoretical conversion to oxides than the W/Na = 0.6 and 2.0 products. Although some sublimate was also observed (Table A-I), it apparently occurred to a much smaller extent. This result suggests that compound formation is occurring, not surprising for $NaW(OEt)_6$(V), but less expected for NaOMe + $W(OMe)_6$ (VI). For the latter an eight coordinate structure might be invoked, but this would require either an additional neutral coordinately bound group, such as a methanol of addition, or the use of bridging alkoxide groups , e.g., $NaW(OMe)_7 \cdot MeOH$ or $Na_2W_2(OMe)_{14}$. For the methanolate compound a theoretical mass loss of 42.4% would be expected compared to the 41.9% observed for the unhydrolyzed and 38.8% for the hydrolyzed. The mass loss for a dimeric double alkoxide complex would be 38.0%, the same as for a monomeric double alkoxide. A dimer could be formed by edge sharing of two eight coordinate square antiprism structures for the tungsten $W(OMe)_7^{-1}$ ions. It is interesting to speculate on the presence of an eight coordinate structure for tungsten. It is uncommon for any oxidation state of tungsten but apparently more uncommon for W(VI). This coordination number is found for the fluoro and cyano compounds, e.g., K_2WF_8 W(VI) and WCN_8^{4-} W(IV)[19]. A closer analog with the potential for eight coordination, but an oxidation state of five, is $WCl_3(OMe)_2 \cdot 3\ MeOH$.[20].

Mass losses observed for the inorganic control melts (Table 2) gave good agreement with the expected values.

3.1.4 Chemical Analysis

Bulk Analysis - Chemical analyses were conducted on starting materials, metal-organic reaction products, and pyrolyzed samples. These measurements were made to assess product purity and to monitor any changes in composition that could arise from treatments of the materials. As noted in the Experimental Section, the analyses proved very difficult, resulting in a lack of confidence in some of the results and consequently confounding their use in interpreting reaction processes. Nevertheless, there is useful information which will be discussed.

The inorganic melts, i.e., the solids prepared by melting mixtures of Na_2CO_3, were made for physical and chemical comparison with corresponding compositions made from metal-organic precursors. These samples were analyzed for sodium and tungsten. The results are given in Table 1. The first four samples have tungsten values which average 3.5% below the expected value based on the weights of the reagent grade chemicals used to make the samples. The sodium values are low on the average by 2.6%. The mass loss observed for the 55:45, $WO_3 : Na_2CO_3$ crucible melt sample was within 1% (i.e., within the precision limit) of the expected value. Analysis of two samples of Na_2WO_4 secondary standards resulted in a repeatability of 0.84% and 0.83% for tungsten and sodium respectively.

The analytical results of the 80:20, $WO_3 \cdot Na_2O$ sample do not agree well with the theoretical values, in fact the tungsten is higher and the sodium lower than expected. This is most likely due to gross inhomogeneities in the sample, based on observations of the physical appearance made during attempts to produce a melt from this tungsten-rich mixture. A similar problem was encountered with the metal-organic precursor 80:20 mixture, i.e., the tungsten value was high and the sodium low.

Regarding the preparation of the metal-organic starting materials, the excellent agreement of the chlorine value for $Cl_2W(OMe)_4$ with the theoretical value (18.68% vs 18.71%) strongly supports the purity of this compound. Although the tungsten value was determined on a different sample, the low value observed (44.72% found versus 48.52% expected) is somewhat surprising. This is especially true since sodium was deliberately added to the unknown prior to the analysis in order to provide the matrix matching which we have found to be important in the AA analysis. An analogous situation is seen for the $W(OMe)_6$ sample where tungsten is about 4% below the expected value. Again, sodium was added to the sample for matrix matching. The amount of sodium added in both cases was that sufficient to equal the amount present in the primary AA tungsten standard, i.e., sodium tungstate, Na_2WO_4, purchased as an aqueous solution standard. Without the addition of sodium to the $Cl_2W(OMe)_4$ and $W(OMe)_6$ samples, during the analytical procedure, the tungsten values measured by AA were 15.5 and 15.8% too high. The fact that both samples, after this procedure modification, now have lower than expected tungsten values may be due to additional matrix effects arising from the presence of the organic constituents. This latter analytical issue was not addressed in the present work, but will be in the analyses of metal-organic calcium tantalate precursors planned for study in Phase II of this contract. It should be noted that the chlorine analysis was done by a wet chemical technique and should not have been as susceptible to the same kinds of interferences as seen for AA.

The sodium and tungsten analyses of all the metal-organic precursor mixtures or compounds and their hydrolysis and/or pyrolysis products are listed in Table 3. It is regrettable that much of the data is not explicable; we can not be positive whether we are seeing unexpected changes in chemical composition or uncertainties in the analyses. The latter possibility could be due to sampling problems with inhomogeneous materials or absolute errors in the AA analysis, due for example, to solution matrix matching effects just mentioned.

The W/Na ratios are probably the most useful expression of the analytical results. Looking at the data from the NaW(OEt)$_6$ series, however, there is no logical explanation why the W/Na ratio should decrease after the sample was autoclaved and dried. There is no apparent mechanism for either a loss of tungsten or a take-up of sodium required to account for this change. Autoclaving the sample and then heating it to 650°C resulted in an increase in the W/Na ratio over that from the starting material, but at 800°C the W/Na ratio found is near that of the starting material. The result for hydrolyzing in humid air and heating to 800°C is expected to, but does not, agree with the autoclaved 800°C sample. Recall (Table 2) that the mass loss observed for the NaW(OEt)$_6$ sample hydrolyzed and heated to 700°C agreed exactly with that predicted by 100% conversion of NaW(OEt)$_6$ to the correspoding sodium tungstate. Thus, on the basis of this data changes in the W/Na ratio with hydrolysis and heat treatments would not be epected.

The analysis of the one to one mixture of NaOMe and W(OMe)$_6$ gave a W/Na ratio close to the expected value and furthemore did not change at all when the dried metal-organic mixture was hydrolyzed and heated to 800°C. This analytical result is not inconsistent with the mass loss data for this system although there is a small difference in mass loss between the hydrolyzed and unhydrolyzed samples, 38.8% versus 41.9% respectively. Thus, the compositional analysis supports possible formation of a one to one chemical complex as suggested earlier.

This line of reasoning, i.e., that of complex formation and inhibition of volatilization, is not supported by the data for the NaOMe + 0.6 W(OMe)$_6$ system. Here one would expect all the W(OMe)$_6$ to be complexed and the non-volatile NaOMe to be in excess. The W/Na ratio found for the pyrolyzed sample however suggests a loss of tungsten. The mass loss observed (Table 2) is higher than expected for 100% conversion to oxides, suggesting volatilization of part of the unhydrolyzed mixture before conversion to non-volatile oxide. The most volatile species present is W(OMe)$_6$. We have no explanation for the high W/Na ratio observed for pyrolysis of the hydrolyzed sample; the pyrolysis mass loss result (Table 2) is close to that expected if all the NaOMe and W(OMe)$_6$ present in the mixture is converted to oxides (38.4% expected versus 40.4% found).

Only one chemical analysis was made of the mixture of two to one tungsten to sodium. This was for the hydrolyzed mixture heated to 900°C. A higher than expected W/Na ratio was found. This would require a loss of sodium, a very unlikely event. The sample may have been sufficiently inhomogeneous that a truly representative portion was not used in the chemical analysis. The mass loss observed from the pyrolysis of the hydrolyzed sample (Table 2) is close to that expected for complete conversion to the corresponding sodium and tungsten oxides.

EDXS Analysis - Energy dispersive x-ray spectroscopy measurements were made on powdered samples from metal-organic precursors (hydrolyzed and unhydrolyzed), the products obtained by melting and solidifying them, and their Na_2CO_3/WO_3 melted and solidified counterparts. Ten particles taken at random were examined from each sample. The irregular shapes of the particles and the weak sodium x-ray signal resulted in Na/W x-ray count ratios of questionable validity. Also, the solids from the crucible melts all had a crystalline appearance. These caveats must be considered when using the standard deviation of the W/Na x-ray count ratio as a possible insight to the degree of compositional inhomogeneity in the samples. The W/Na x-ray count ratios, calculated and found, and the standard deviations for all the samples examined are reported in Table 4.

3.2 Gel Formation (Liquid Water Hydrolysis)

The formation of a gel precursor, in our case from a solution of tungsten and sodium alkoxides, is the most desirable metal-organic route to the preparation of homogeneous sodium tungstates. If gelation is successful, the glass precursor components are mixed on a molecular scale (at least at the instant of gelation), many of the metal-oxygen-metal bonds of the final oxide product have already been formed, and most of the alkoxy groups have been cleaved. The cross linked gel structure should also be susceptible to further hydrolysis by water vapor after its initial drying.

Silicon alkoxides readily gel from hydrolysis at room temperature, especially in the presence of a catalyst. When other metal alkoxides are present, synthesis conditions become more difficult due to preferential hydrolysis; this often results in precipitation of one or more components before gelation, resulting in a compositionally inhomogeneous product. We have, however, prepared clear transparent gels with up to five metals without precipitation, using silicon ethoxide as the gel former and ethoxide derivatives for the other metals. Germanium alkoxides, on the other hand, readily form precipitates when hydrolyzed at room temperature, without the use of a catalyst. Nevertheless, we have succeeded in producing a gel from germanium ethoxide by working under cryogenic conditions. The preparation of a homogeneous gel from germanium akoxides is even more difficult when other metal alkoxides are present.

We expected tungsten alkoxides to behave more like germanium alkoxides, i.e., the relatively large tungsten atom gives an alkoxide structure with little steric hindrance to an attack by a water molecule and the tungsten-oxygen bound should be highly polarized. facilitating cleavage with water. We tried to find conditions to gel the tungsten hexamethoxide compound before trying a mixture of it with sodium alkoxide. The formation of a gel instead of a precipitate depends, in part, on determining the correct amount of water to add during hydrolysis, i.e., the H_2O to W ratio. Adjusting (usually lowering) the temperature of the solution is another way to inhibit precipitate formation during hydrolysis.

The simplest system we examined was tungsten hexamethoxide dissolved in methanol. We found that precipitation during hydrolysis would not occur if the solution was cooled to -18°C during the water addition. Using a water to tungsten ratio of 1.0 resulted in a clear solution, which remained clear at room temperature. Increasing the water to tungsten ratio to 2.0 resulted again in a clear solution at -18°C but a dark blue solution with a dark blue precipitate formed when the solution was warmed to room temperature. The precipitate formation under those conditions indicated that the hydrolysis reaction,

$$W(OMe)_6 + H_2O \longrightarrow W(OMe)_{6-x}(OH)_x + x\ MeOH \qquad (\ )$$

occurred much more rapidly than the polymerization reaction.

$$W(OMe)_6 + W(OMe)_{6-x}(OH)_x \longrightarrow (MeO)_5\ W\text{-}O\text{-}W(OMe)_{6-x}(OH)_{x-1} \qquad (6)$$

The hydrolysis reaction rate can be decreased by increasing the size of the alkoxy group and thereby increasing steric hindrance toward attack of the tungsten atom by a water molecule. This was the motivation for replacing methoxy groups with isopropoxy groups. Using isopropanol solvent, the product obtained by $i\text{-}C_3H_7OH$ exchange with $W(OMe)_6$ was very soluble at elevated temperatures, but only slightly soluble at room temperature. Water was added at 28°C until at $H_2O/W = 1.00$ a clear solution with a white precipitate resulted. The precipitate would not dissolve when the mixture was heated.

Despite this lack of success in producing a gel from tungsten methoxide and isopropoxide we did attempt a hydrolysis of a tungsten methoxide-sodium methoxide solution in methanol. Hydrolysis was carried out at room temperature since solubility was a problem at lower temperatures. With $H_2O/W = 1.0$ a clear solution with a white precipitate resulted.

We have hardly exhausted the techniques to make a gel, e.g., very bulky alkoxy groups such as t-butoxy may permit a more controlled hydrolysis and result in a polymerized tungsten-oxygen-tungsten network. Nevertheless, our lack of success in forming a gel is discouraging when considering this approach for the preparation of homogeneous starting materials for containerless processing.

3.3 Containerless Melting (Drop Tower Experiments)

Containerless melting experiments were conducted by rapidly heating and rapidly quenching metal-organic and inorganic oxide precursor powders during free fall in a 3.9 m drop tower furnace. These experiments had a higher probability of success for glass formation than those described in Section 3.1 since sodium tungstate glasses have been synthesized from conventional starting materials using rapid quench techniques [15,16].

Using an inorganic feed material, 65:35 WO_3:Na_2CO_3, we obtained clear beads from our drop tower experiments, when the starting particles were sufficiently small to undergo melting during their fall through the furnace. The clear colorless beads became opaque between 300°C and 350°C when heated in a box furnace. This qualitative evidence of devitrification is in reasonably good agreement with the reported T_c of 353° [5] for 65:35 WO_3:Na_2O, and supports our assumption that these beads are amorphous sodium tungstate.

Clear beads were also made from metal-organic materials. However black spheres, white spheres, and black particles were also present which made it difficult to isolate and remove the clear beads for further study, i.e., determination of Tc. A small number of clear beads from several samples were heated in a box furnace and the temperauture at which opacity, and presumably devitrification, occurred was noted. Except for the W/Na = 0.6 sample, opacity was not observed until 350°C. An estimate of the fraction of shells which changed from clear and colorless to opaque and white is given in Table 5. For the W/Na=0.6 sample some opacity was seen at 200°C and about one half of the beads became opaque at 325°C.

The white spheres may indicate devitrification while the black spheres and particles imply that not all the carbon has been removed from the metal-organic powders. The size range of the particles dropped through the tower was not sufficiently narrow nor was the experiment sufficiently controlled to allow a correlation to be made between particle size and the extent of clear bead or black sphere formation. This was mainly due to the small amount of sample available for these experiments. The materials examined, the furnace temperatures used and a qualitative description of the appearance of the products obtained are reported in Table A-11. Hydrolyzing the metal-organic materials and/or raising the temperature of the drop tower furnace seemed to increase the fraction of clear beads in the samples.

Although we have no explanation for the results, it is interesting to note the differences between the drop tower furnace products obtained from the W/Na = 0.6 material and those from the W/Na = 2.0 material. The former gave only clear, presumably glassy, beads or flattened melts, while the latter gave only discolored, black products, although; 1) the starting materials in both cases were hydrolyzed to assist in removal of organic groups 2) the particle sizes were similar and 3) the furnace was at the same relatively high temperature of 1000°C. Tatsumisago et. al.[15] report the W/Na = 0.6 oxide material to be on the lower boundary of the compositional range for glass production by rapid quenching using chilled rollers.

The W/Na = 1 material gave a mixture of products intermediate between the other two.

The beads or spheres produced from these experiments have a consistent fixed geometry, i.e. spherical, and is one with which we are very familiar from our glass shell analyses. They are perhaps the next best thing to polished flats for EDXS analysis. EDXS analysis of these products, and additional corresponding inorganic melts, may permit determination of the homogeneity of metal-alkoxide derived glasses versus that of glasses from conventionally mixed tungsten oxide and sodium carbonate, both produced by containerless melting. These experiments have yet to be done.

A surprising result seen in all the drop tower experiments, with metal-organic precursors, was the presence of hollow glass spheres (in very low yields). An example of these shells is shown in Figure 3. The role of residual carbon in the material, whose oxidation product(s) is presumably the shell blowing gas, is shown by the absence of shell formation with the WO_3/Na_2CO_3 starting material.

Shell formation in the sodium tungsten system is particularly noteworthy since glass shells containing high atomic number elements have been of recurring interest to the inertial confinement fusion community and constitutes a potentially significant spin-off from this study.

4. Summary and Conclusions

The inability to form a gel from tungsten alkoxides (methoxide and isopropox compromised considerably the ability to produce homogeneous metal-organic precursors for sodium tungstates. Although further work might eventually lead to a gel, our attempts using hydrolysis at low temperatures, resulted only in precipitate formation.

Three tungsten-sodium systems were examined using 0.6, 1.0 and 2.0 molar ratios of $W(OMe)_6$ to NaOMe in methanol. These alkoxides in methanol solution gave initially homogeneous mixtures i.e., solutions, but evaporation of the solvent produced products of unknown homogeneity. Pyrolysis of the direct alkoxide mixtures resulted in greater than expected weight losses for the W/Na = 0.6 and 2.0 mixture suggesting preferential evaporation (sublimation) of $W(OMe)_6$ before decomposition. The W/Na = 1.0 mixture had a weight loss close to that expected for conversion to the correspondingly oxide mixture. This observation and the constant W/Na ratio found by chemical analysis of the mixture pyrolyzed to 800°C suggest compound formation. The known compound $NaW(OEt)_6$, with W(V), behaved similarly when pyrolyzed, i. e., the mass loss was close to that expected for complete conversion to oxide. In all cases however, the presence of gray, brown or black particles in the pyrolyzed products indicated the presence of reduced carbon which was not removed until about 500°C. Although low temperature (200° - 300°C) pyrolysis of the W/Na = 1 and W/Na = 2 mixture from $W(OMe)_6$ and NaOMe gave some glassy products we must concede that we were unsuccessful in producing a homogeneous glass without melting.

Hydrolysis of the dried metal alkoxide mixtures with water vapor (humid air) succeeded in preventing the loss of tungsten upon subsequent heating. The mass losses of the hydrolyzed materials corresponded closely with that expected for complete conversion to oxide. Also, as a result of this hydrolysis there was a considerable reduction in the amount of discoloration seen in the metal-organic precursors during pyrolysis. Unfortunately the organic groups were not completely removed since some discoloration remained until the mixtures were heated above 500°C. Again, no homogeneous glasses were formed at temperatures below the liquidus, but the W/Na = 1 mixture from $W(OMe)_6$ and NaOMe gave a light gray glassy product at 400°C.

Experimental results with the drop tower furnace were somewhat more encouraging with respect to glass formation. When dropped through a 3.9 m furnace at 800-1000°C a mixture of products was generally produced from the hydrolyzed metal-organic precursors. Some black particles were present in most samples, but all except the W/Na = 2 sample also yielded some clear colorless beads, strongly suggesting the formation of a glassy phase. This assumption was confirmed by heating the clear colorless beads in a box furnace during which they became opaque in substantially the same temperature region reported for T_c of sodium tungstate prepared from inorganic precursors.

The analysis of the metal alkoxide precursor powders and their oxidized products. by atomic absorption spectrometers was made difficult by interferences of the metals, sodium and tungstun with each other, and, we suspect, the presence of organic constituents. Some analyses gave good agreement with the expected values while others differed considerably from expected values. Although we are switching metals for the second phase of this work (to calcium tantalates) the experience gained here should be useful in future analyses. We can propose no logical explanation for the EDXS analyses of the metal-organic products since some exceptions always existed for every trend that could be postulated. An EDXS analysis of the clear beads might provide more accurate information on the compositional homogeneity of the products, but not enough time was available to continue this study.

The formation of shells in the drop tower experiment was a very interesting development which may be of future use in ICF target fabrication.

Finally, we are forced to conclude that unless homogeneous sodium-tungsten gels can be produced (which we have thus far been unable to do) we can see no particular advantage to the use of metal-organic precursors as a route to sodium tungstates in containerless processing.

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Table 1.

AA Analyses of Sodium Tungstates Prepared from WO_3 and Na_2CO_3

Nominal Composition Mole %		Wt. % Element				W/Na Mole Ratio	
		Tungsten		Sodium			
WO_3	Na_2O	Calc	Found	Calc	Found	Calc	Found
54	46	64.4	62.2	13.7	13.4	0.59	0.575
55	45	64.9	62.8	13.5	13.5	0.60	0.575
67	33	69.9	67.4	8.8	8.4	0.99	1.00
68	32	70.6	68.0	8.2	7.9	1.07	1.07
80	20	74.2	79.5	4.8	3.8	1.94	2.60

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* Calculated on the basis of amounts of WO_3 and NA_2CO_3 used in melting experiment.

Table 2

Mass Losses During Pyrolysis

Material	Total Mass Loss,% Observed	Expected [a]	Pyrolysis Temp., °C
NaOMe + 0.6 $W(OMe)_6$	52.6	38.4	800
NaOMe + 0.6 $W(OMe)_6$, Hydrolyzed[b]	40.4		700
NaOMe + $W(OMe)_6$	41.9	38.0	800
NaOMe + $W(OMe)_6$, Hydrolyzed[b]	38.8		800
$NaW(OEt)_6$	47.2	45.6	700
$NaW(OEt)_6$, Hydrolyzed[b]	45.6		700
NaOMe + 2$W(OMe)_6$	55.7	37.7	800
NaOMe + 2$W(OMe)_6$, Hydrolyzed[b]	36.3		900
55:45 WO_3/Na_2CO_3	11.6	11.6	700
80:20 WO_3/Na_2CO_3	4.5	4.3	1000

a) Expected for 100% conversion of sodium and tungsten to Na_2O and WO_3.
b) Hydrolyzed by exposure to water vapor in a humidity chamber.

Table 3

Chemical Analysis of Metal-Organic Compounds and their Decomposition Products

	Wt. % of Element				W/Na Mole Ratio		Total
	Tungsten		Sodium				
	Calc	Found	Calc	Found	Calc	Found	Na_2O + WO_3
$NaW(OEt)_6$	42.5	42.18	5.3	5.94	1.0	0.89	
$NaW(OEt)_6$, autoclaved, dried		53.98		8.52	1.0	0.79	
$NaW(OEt)_6$, autoclaved, 650°	69.9	62.3	8.7	5.35	1.0	1.46	90.6
$NaW(OEt)_6$, autoclaved, 800°	69.9	70.3	8.7	10.12	1.0	0.87	101.8
$NaW(OEt)_6$, humid air, 800°	69.9	64.1	8.7	10.10	1.0	0.79	94.4
NaOMe + $W(OMe)_6$	37.6	41.7	48	5.02	0.98	1.04	
NaOMe + $W(OMe)_6$, humid air, 800°	69.8	65.9	8.9	7.86	0.98	1.04	93.3
NaOMe + 0.6 $W(OMe)_6$	35.0	36.7	7.3	6.89	0.60	0.67	
NaOMe + 0.6 $W(OMe)_6$, 800°	64.9	59.8	13.5	15.2	0.60	0.49	96.0
NaOMe + 0.6 $W(OMe)_6$, humid air, 700°	64.9	67.9	13.5	11.1	0.60	0.76	100.6
NaOMe + 2 $W(OMe)_6$, humid air, 900°	74.4	78.1	4.6	4.08	2.0	2.39	104.0

Table 4

Ratio of W/Na X-ray Counts and Their % SD for All Samples Studied

Material	Theory	Found[a)]	S.D. %
NaOMe + 0.6 $W(OMe)_6$	.208	.293	85
NaOMe + 0.6 $W(OMe)_6$, 800°	.208	.146	8
NaOMe + 0.6 $W(OMe)_6$, hydrolyzed	.208	.209	47
NaOMe + 0.6 $W(OMe)_6$, hydrolyzed, 700°	.208	.127	15
Na_2CO_3 + WO_3, 700°	.208	.116	19
NaOMe + $W(OMe)_6$	.125	.155	38
NaOMe + $W(OMe)_6$, 800°	.125	.0670	23
NaOMe + $W(OMe)_6$, hydrolyzed	.125	.129	9
NaOMe + $W(OMe)_6$, hydrolyzed, 800°	.125	.0556	16
Na_2CO_3 +WO_3, 950°	.125	.0924	15
NaOMe + 2 $W(OMe)_6$	.0625	.120	44
NaOMe + 2 $W(OMe)_6$, 800°	.0625	.0582	21
NaOMe + 2 $W(OMe)_6$, hydrolyzed	.0625	.0615	38
NaOMe + 2 $W(OMe)_6$, hydrolyzed, 900°	.0625	.0246	42
Na_2CO_3 + WO_3, 950°	.0625	.0390	29
$NaW(OEt)_6$, 800°	.125	.107	16

a) Based on the analysis of 10 particles.

Table 5

Devitrification Behavior of Glassy Beads Produced from Hydrolyzed Metal-Organic Precursors in a Drop Tower Furnace

Material	Furnace Temperature($^{\circ}C$)	Estimate of % Opaque and White Beads at $350^{\circ}C$
$NaW(OEt)_6$, Hydrolyzed	800	90
$NaOMe + W(OMe)_6$, Hydrolyzed	800	70
$NaOMe + W(OMe)_6$, Hydrolyzed	1000	35
$NaOMe + 0.6\ W(OMe)_6$, Hydrolyzed	1000	100

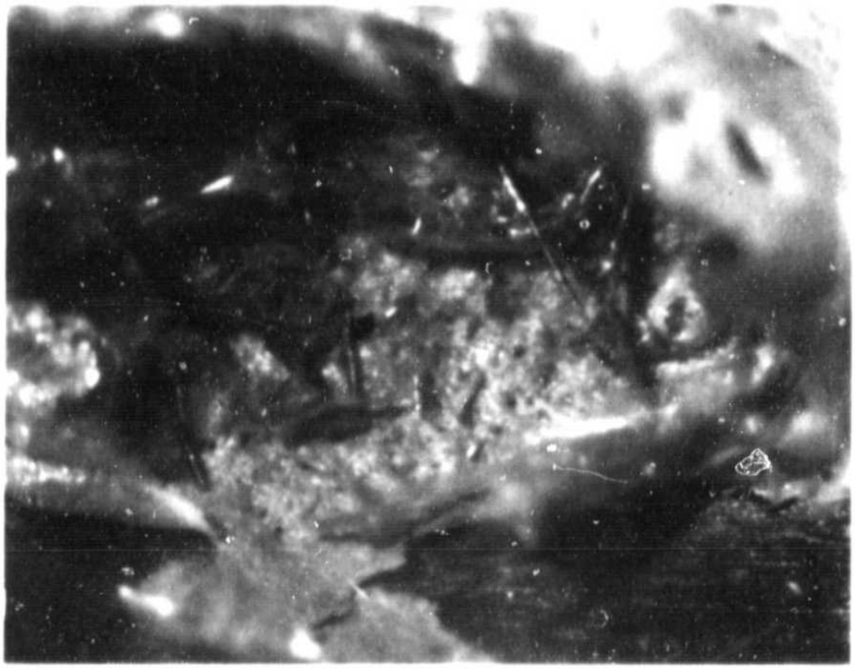

Figure 1. Optical photomicrograph of a $2W(OMe)_6 \bullet NaOMe$ sample heated to 200°.

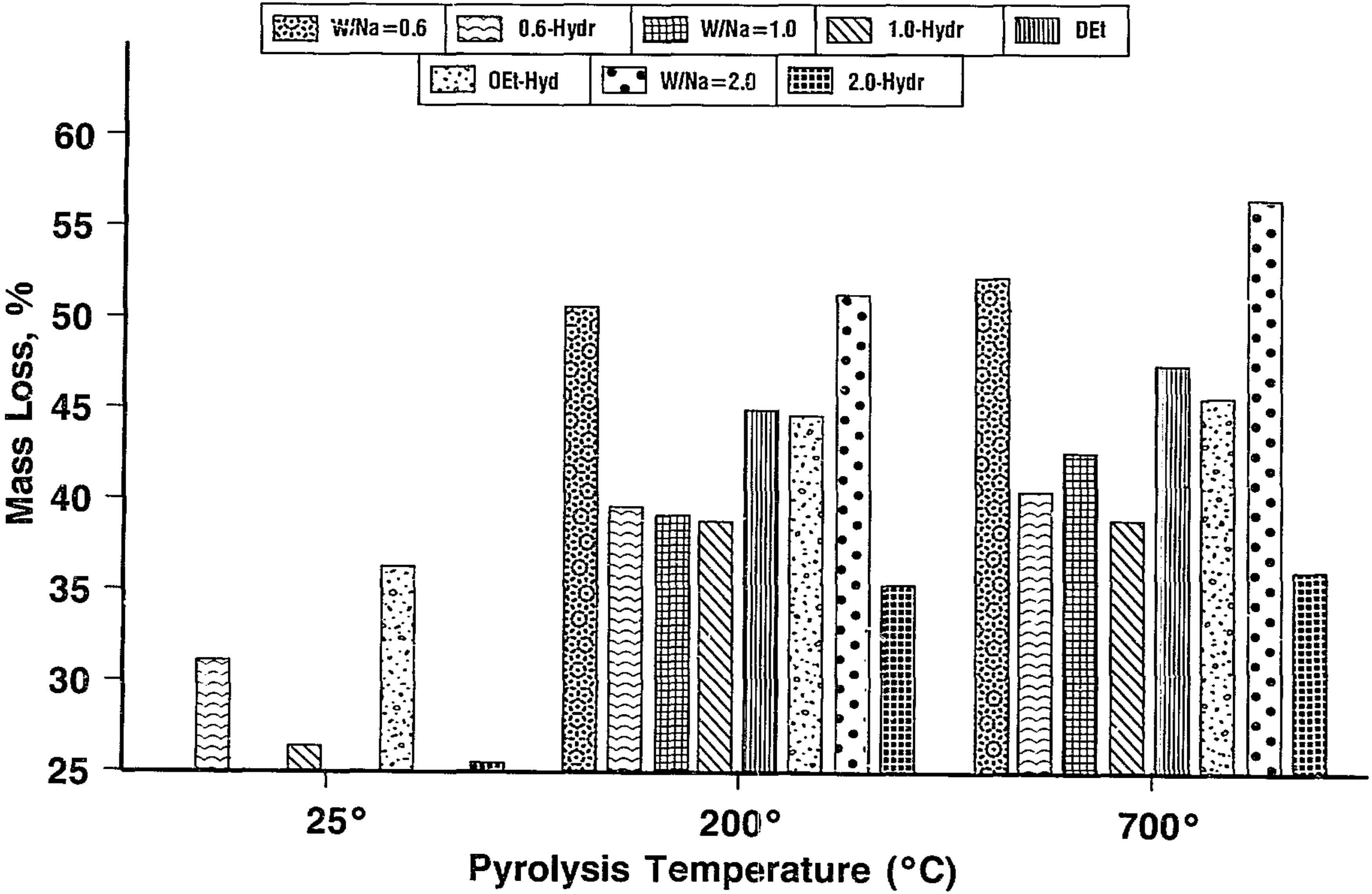

Figure 2. Mass loss of metal-organic products by Pyrolysis—all compounds are methoxides, except "OEt" means $NaW(OEt)_6$.

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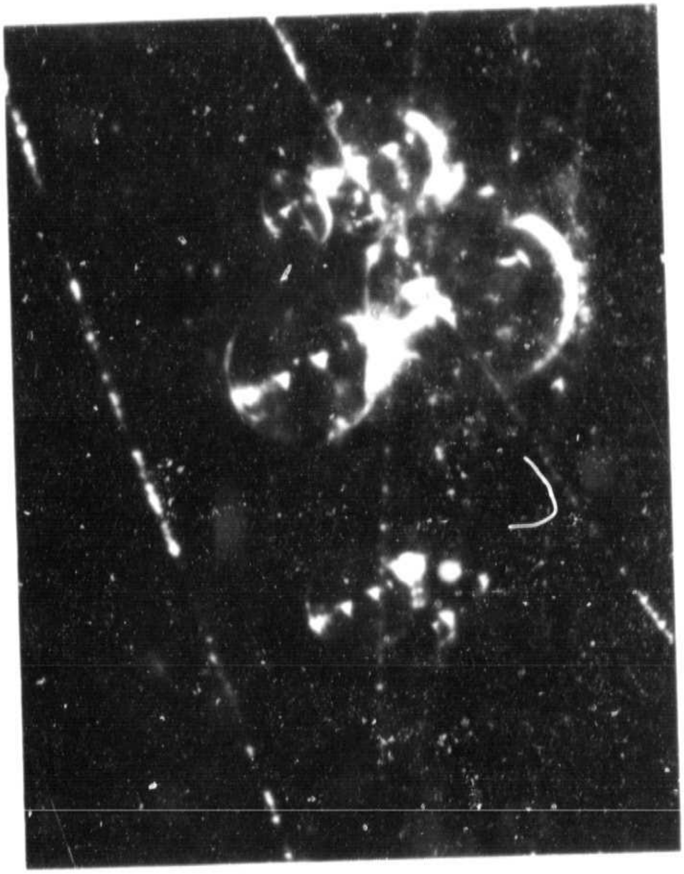

Figure 3. Glass shells produced in a drop tower at 1000° from metal-organic sodium tungstate precursor.

Appendix

The following tables provide detailed information on the mass losses observed at 100° intervals for various pyrolyzed sodium tungstate samples. In addition, brief descriptions are given of the physical appearance of the materials at each heating stage for crucible melts and at several furnace temperatures for products obtained from drop tower experiments.

Table A-I

Pyrolysis of the $NaOMe/0.6W(OMe)_6$ Reaction Product (W/Na = 0.6)

Treatment Temperature (°C)	% wt loss	Comment
200	50.5	Dark brown & light brown particles. Some sublimation with black color.
300	50.4	Dark brown & light brown particles. Dark brown seeds present.
400	51.0	Little change except light brown now predominating.
500	52.4	Dark brown & ivory particles. Seeds are light brown. Sublimate is yellow.
600	51.6	Ivory colored coral structure. Parts of it reflect light.
700	51.8	Melted, milky white. Reflects light.
800	52.3	More flow occurred. Some flaking up from crucible.

Table A-2

Pyrolysis of the NaOMe/W(OMe)$_6$ Reaction Product (W/Na = 1)

Treatment Temperature, °C	% Mass Loss	Comment
200	39.1	Gray color. Some sublimation with black color.
300	39.7	Material is mostly brown with glassy appearance.
400	41.0	More brown, but still glassy.
500	41.2	Black, not so glassy. Sublimate is yellow.
600	4[illegible]	Mostly white.
700	42.4	All white, crystals present.
800	41.9	Melted, large crystals.

Table A-3

Pyrolysis of $NaW(OEt)_6$ (W/Na = 1)

Treatment Temperature (°C)	% wt loss	Comment
200	44.8	Brown with black on top. Brown sublimate.
300	45.9	Brown with black on top. Brown sublimate.
400	46.6	Brown with black on top. Sublimate is yellow.
500	47.2	Ash colored. White coating on black film.
600	47.4	White and dark gray powder.
700	47.2	White crystalline melt.

Table A-4

Pyrolysis of the $NaOCH_3 + 2\ W(OCH_3)_6$ Reaction Product (W/Na=2)

Treatment Temperature (°C)	% wt loss	Comment
200	51.3	Top surface melted, brown color. Some of surface peeled and is transparent. Sublimation on lid and sides with black color.
300	53.1	Mainly black. Peels are still transparent.
400	56.2	Mainly black. Peels are still transparent. Sublimate mostly yellow.
500	55.2	Yellow white material. Peels are slightly transparent.
600	55.4	Mainly white. Peels are no longer transparent.
700	56.4	Mainly white. Peels are no longer transparent.
800	55.7	Light blue crystalline melt.

Table A-5

Pyrolysis of 55:45 WO_3/Na_2CO_3 (W/Na = 0.6)

Treatment Temperature (°C)	% wt loss	Comment
None	-	Green powder.
200	0.6	Green powder.
300	0.1	Green powder.
400	0.1	Green powder.
500	1.0	Yellow-green powder.
600	3.8	Yellow-green particles and white particles.
700	11.6	Milky-white crystalline melt.

Table A-6

Pyrolysis of 80:20 WO_3/Na_2CO_3 (W/Na = 2)

Treatment, °C	% wt loss	Comment
None	-	Yellow-green powder.
200	0.5	Yellow-green powder.
300	0.2	Yellow-green powder.
400	0.1	Yellow-green powder.
500	0.6	Yellow-green powder with a few white particles.
600	4.5	Yellow-green powder with many white particles.
700	4.5	Approx. 60% yellow-green, approx. 40% white.
800	4.5	Mainly white with some green spots and some black spots.
900	4.5	Very dark green with white crystals.
1200	4.5	Dark green crystals and white crystals.
1100	10.7	Dark green crystals and white crystals.
1200	12.4	Dark green crystals and white crystals.
1200	13.0	Dark green crystals and white crystals reheat.

Table A-7

Pyrolysis of the Hydrolyzed NaOMe + 0.6 $W(OMe)_6$ Reaction Product (W/Na=0.6)

Treatment Temperature (°C)	% wt loss	Comment
Hydrolysis	31.2	White powder.
200	39.3	White powder.
300	40.6	White powder.
400	40.5	Gray powder.
500	40.3	Gray powder.
600	40.5	Gray powder.
700	40.4	Milky-white crystalline melt.

Table A-8

Pyrolysis of the Hydrolyzed NaOMe + $W(OMe)_6$ Reaction Product (W/Na = 1)

Treatment Temperature, °C	% wt loss	Comment
Hydrolysis	26.3	White, glassy.
200	38.6	Ivory, glassy
300	38.5	Light gray with some dark gray regions. Glassy regions.
400	38.7	Light gray, glassy.
500	38.7	Light gray, glassy.
600	38.8	White, no longer glassy
700	38.7	White, shrinkage occurred.
800	38.8	Melt. Yellow crystals.

Table A-9

Pyrolysis of Hydrolyzed $NaW(OEt)_6$ (W/Na = 1)

Treatment Temperature, °C	% wt loss	Comment
Hydrolysis	36.2	White powder.
200	44.5	Brown to light brown.
300	44.3	Brown to light brown.
400	45.2	Brown to light brown.
500	44.4	Dark gray.
600	45.8	Very light gray - like ashes. Free flowing powder.
650	45.8	Partially melted. White color.
675	45.7	Partially melted. White color.
700	45.6	White crystalline melt.

Table A-10

Pyrolysis of the Hydrolyzed NaOMe + 2 $W(OMe)_6$ Reaction Product (W/Na = 2)

Treatment Temperature (°C)	% wt loss	Comment
Hydrolysis	25.4	White powder.
200	35.2	Light brown powder, with some clear melts.
300	35.5	Light brown powder, with some clear melts.
400	36.4	Yellow and dark gray particles. Melts are dark and opaque.
500	35.3	Yellow gray powder. Melts turning white.
600	35.5	Yellow and white. White part is sintered.
700	36.0	Yellow and white. White part is sintered.
800	36.1	Free flowing powder. White pieces and green pieces. White part is sintered.
900	36.3	Very dark green melt.

Table A-11

Drop Tower Experiments

Drop Tower Run No. T4R	Material	Temp. °C	Result - Physical appearance of products
102	65:35 WO_3/Na_2CO_3 Powder	800	Clear beads, large unmelted particles. $T_c = 300^\circ$-350°.
103	$NaW(OEt)_6$	800	Clear beads, black spheres, black particles.
104	$NaW(OEt)_6$, Hydrolyzed	800	Same.
105	$NaW(OEt)_6$, Hydrolyzed	900	Same.
106	NaOMe + $W(OMe)_6$	800	Clear beads, white spheres, black beads, black particles.
107	NaOMe + $W(OMe)_6$, Hydrolyzed	800	Same.
108	NaOMe + $W(OMe)_6$, Hydrolyzed	900	Same.
109	NaOMe + $W(OMe)_6$, Hydrolyzed	1000	Same.
110	NaOMe + 0.6 $W(OMe)_6$, Hydrolyzed	1000	Clear beads and splats.
111	NaOMe + 2 $W(OMe)_6$, Hydrolyzed	1000	Black spheres and black particles.