

Fiber Optical Micro-detectors for Oxygen Sensing in Power Plants

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ABSTRACT

A reflection mode fiber optic oxygen sensor that can operate at high temperatures for power plant applications is being developed. The sensor is based on the $^3\text{O}_2$ quenching of the red emission from hexanuclear molybdenum chloride clusters. One of the critical materials issues is to demonstrate that the luminescent cluster immobilized in the sol-gel porous support can withstand high temperature. At the same time the sol-gel matrix must have a high permeability to oxygen. Using a potassium salt of the molybdenum clusters, $\text{K}_2\text{Mo}_6\text{Cl}_{14}$, we have established the conditions necessary for deposition of optical quality sol-gel films. From spectroscopic measurements of the film we have shown that the cluster luminescence is stable following heat cycling of 1 hour at 250°C . Quenching of a factor of 4X between pure nitrogen and 21% oxygen was observed for films cured directly at 200°C . These are promising results for a high temperature fiber optical oxygen sensor based on molybdenum chloride clusters.

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INTRODUCTION

Maximizing the efficiency of the combustion process requires real-time control of the correct fuel/oxygen ratio. This requires the ability to sense oxygen levels over a broad range of concentrations with fast response times. Mussell, Newsham, and Ruud previously reported preliminary studies of the synthesis and optical properties of $\text{Mo}_6\text{Cl}_{12}$ -based clusters relevant to this project ^[1-4]. Mussell described the synthesis of the molybdenum clusters, and Newsham gives a good account of the properties of neutral $\text{Mo}_6\text{Cl}_{12}$ clusters and their salts, in both solution and a sol gel matrix. Newsham's data indicate that the photophysical properties of the clusters are maintained in sol gel matrices. To prepare a fiber optic sensor based on $\text{Mo}_6\text{Cl}_{12}$, Ruud dispersed $\text{Mo}_6\text{Cl}_{12}$ in poly[1-trimethylsilyl-1-propyne] (PTMSP), and used a dipping technique to immobilize the composite at the cleaved end of a silica optical fiber. Ghosh and co-workers ^[5] demonstrated a fast room temperature fiber optic sensor based on oxygen quenching of the luminescence from the PTMSP/ $\text{Mo}_6\text{Cl}_{12}$ composites. While the PTMSP support is adequate for room temperature applications, is unable to withstand the high temperatures associated with combustion in a power plant. To improve the sensor's high temperature performance, we are replacing PTMSP with a thermally stable sol gel matrix that should be able to withstand the higher temperature requirements of the power plant combustion process. The idea of using a sol gel as the support matrix for high temperature oxygen sensor application is not new. Remillard and coworkers have shown that a sol gel supported copper based oxygen sensor can be used in a combustion process ^[6]. With these facts in hand, we anticipate promising results from our design.

EXECUTIVE SUMMARY

A requirement of optical sensors based on luminescence quenching is that the lumophore have a strong luminescence that is efficiently quenched by oxygen, and that oxygen has ready access to the lumophore. For a high temperature sensor, these characteristics must hold over the entire temperature range of interest. Since the maximum luminescence intensity of a lumophore at high temperatures is related to its intrinsic stability, a key goal for the previous quarter was to define the intrinsic thermal stability of $\text{K}_2\text{Mo}_6\text{Cl}_{14}$, the potassium salt of $\text{Mo}_6\text{Cl}_{12}$. In this work, we carried out isothermal aging experiments where we measured the change in sample weight at a constant temperature as a function of time. These are essentially accelerated aging studies that can be used to estimate the long term stability of $\text{Mo}_6\text{Cl}_{12}$ and $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ clusters at lower temperatures.

We also characterized the stability of lumophore/sol-gel composites following temperature cycling. We thermally stressed a $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ / sol-gel film by curing it for one day at 70°C , followed by a 2 hour anneal at 150°C , then a 1 hour anneal at 200°C , then a 1 hour annealed at 250°C , and finally 1 hour anneal at 300°C . The luminescence signal in nitrogen is unchanged through the 250°C thermal cycling, then begins to degrade following the 300°C anneal. These spectroscopic results agree with thermal gravimetric analysis of the potassium salt itself. However, the quenching ratio (luminescence intensity in 99.999% N_2 compared to 21% O_2) decreased with temperature. This problem was solved by curing the $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ / sol-gel film directly at 200°C for 30 minutes. A strong luminescence signal was observed from two independently processed samples, along with a quenching ratio of 3.5 - 4.0X. Both the luminescence intensity and quenching numbers are favorable for fabrication of a high temperature fiber optic sensor.

From a project management perspective, a new postdoctoral researcher, Dr. Po Zhang, joined the project on Nov. 1, 2004. Dr. Zhang has a PhD in Electrical and Computer Engineering from Virginia Polytechnic Institute. He has academic and industrial experience in optical fiber sensors, including previous DOE/NETL projects on optical pressure and temperature sensors for oil wells. Dr. Zhang is working on spectroscopic and optical fiber sensor development portion of the program.

During the current reporting period, a patent disclosure entitled "Sol-gel encapsulated hexanuclear clusters for oxygen sensing by optical techniques" was submitted to the Michigan State University intellectual property department. We expect to submit the provisional patent application in January 2005.

EXPERIMENTAL

Materials.

All glassware was oven-dried prior to use. Acetonitrile (Spectrum Chemical Company, HPLC grade) was dried over CaH_2 and distilled prior to use. Tetraethyl orthosilicate (TEOS) (Aldrich, 98%) and hydrochloric acid (CCI, electronics grade) were used as received. Corning 7980 quartz microscope slides ($3'' \times 1'' \times 1 \text{ mm}$) were obtained from Technical Glass Products and cut into $1.25 \text{ cm} \times 2.45 \text{ cm}$ pieces. Slides were handled with gloves and tweezers in order to minimize surface contamination.

Preparation of the $\text{Mo}_6\text{Cl}_{12}$ hydrochloride salt.

MoCl_2 from City Chemical (lots 40C65 and 40M21) was received as a yellowish-green powder with small dark-blue specks and was purified by conversion to the $\text{Mo}_6\text{Cl}_{12}$ hydrochloride salt. A representative procedure is described. MoCl_2 (2g) and 800 mL of 6M HCl were added to a 1 L Erlenmeyer flask and stirred with a Teflon coated magnetic stir bar. The solution was heated to the boiling point for several hours and the resulting bright-yellow solution was then filtered through medium-fast filter paper to remove insoluble white and metallic particles. The filtered solution was heated on a hot plate and the volume reduced to 200 mL. The hot plate was turned off and the solution was left on the hot plate to slowly cool to room temperature. A small amount of seed crystals were added and yellow crystals formed overnight. After cooling the solution in an ice bath for 5 hours, the resulting yellow crystals of the hydrochloride salt were collected by gravity filtration through Whatman medium-fast filter paper. The crystals were then placed onto several pieces of filter paper and allowed to dry under ambient conditions for two days. Yield: 586 mg. A second crop of crystals was obtained by heating to concentrate the mother liquor to 100 mL, filtration, and a further reduction in volume to 50 mL. Cooling, seeding the solution as described above, and storing the solution in a freezer overnight yielded long yellow needles. Drying the needles on filter paper yielded 256 mg of the $\text{Mo}_6\text{Cl}_{12}$ hydrochloride salt. The products were characterized using x-ray powder diffraction, uv-vis spectroscopy, fluorescence spectroscopy, and energy dispersive x-ray spectroscopy.

Preparation of the potassium salt of $\text{Mo}_6\text{Cl}_{12}$. ($\text{K}_2\text{Mo}_6\text{Cl}_{14} \cdot 2\text{H}_2\text{O}$, sample FJ-17)

A KCl solution in HCl (50 mL, prepared by dissolving KCl (0.2533g, 0.214 mmol) in 50 mL of 6M HCl) was added to an Erlenmeyer flask containing a stirred solution of $\text{Mo}_6\text{Cl}_{12}$ (300 mL, $2.90 \times 10^{-3} \text{ M}$) in 6M HCl. The resulting yellow solution was concentrated to 100 mL by boiling on a hot plate with stirring. The solution was slowly cooled to room temperature on the hot plate, stoppered and placed in a refrigerator. The resulting yellow needles were collected by gravity filtration through Whatman medium-fast filter paper. The crystals were then spread onto several pieces of filter paper and allowed to dry under ambient conditions, to give 613.2 mg of bright yellow crystals. The products were characterized using x-ray powder diffraction, uv-vis spectroscopy, fluorescence spectroscopy, and energy dispersive x-ray spectroscopy. For simplicity, FJ-17 (prepared from City Chemical lot 40C65) is referred to in this report as “salt A”.

Preparation of the potassium salt of $\text{Mo}_6\text{Cl}_{12}$. ($\text{K}_2\text{Mo}_6\text{Cl}_{14}\cdot 2\text{H}_2\text{O}$, MM5)

A saturated KCl solution was prepared by adding KCl to hot 6M HCl (900 mL). Upon cooling, the excess KCl precipitated and the supernatant was decanted from the precipitated salt. Similarly, a saturated solution of $\text{Mo}_6\text{Cl}_{12}\cdot 2\text{HCl}$ was prepared in 400 mL of 6M HCl. The two solutions were combined at room temperature in a 2L Erlenmeyer flask. After ~20 minutes, precipitation of the yellow product was complete, and the powder was isolated by gravity filtration through Whatman medium-fast filter paper. After rinsing with 20 mL of cold 6M HCl, the powder was placed on several pieces of filter paper and allowed to dry under ambient conditions, to give 966 mg of bright yellow crystals. The products were characterized using x-ray powder diffraction, uv-vis spectroscopy, fluorescence spectroscopy, and energy dispersive x-ray spectroscopy. For simplicity, MM5 (prepared from City Chemical lot 40M21) is referred to in this report as “salt B”.

Film Deposition.

Sol-gel films were deposited on quartz slides to assess the importance of variables that might affect long-term thermal stability and improve quenching. Slides were washed with distilled water, soaked in 2.0 M aqueous KOH, rinsed with distilled water for at least 1 hour, and stored in distilled water.

A typical stock sol-gel solution for the coating process was prepared as described below. TEOS (100 mL, 0.477 mol) and acetonitrile (70.3 mL) were added to a 500 mL Erlenmeyer flask. With stirring, water (32.3 mL, adjusted to pH=1 with HCl) was added and the solution was stirred for 1 hour at room temperature. The stir bar was removed from the flask and the solution was heated in an oil bath at 70 °C for 2.5 hours. The solution was then transferred to a 500 mL glass bottle, capped, and aged at room temperature until use. For the 29 series of samples, 25.5 mg of $\text{K}_2\text{Mo}_6\text{Cl}_{14}\cdot 2\text{H}_2\text{O}$ was added to the vial approximately three days before dipping the slides, and the solution was stirred for three days to ensure complete dissolution of the complex. For the 30 series of samples, the process was identical except 62.2 mg of $\text{K}_2\text{Mo}_6\text{Cl}_{14}\cdot 2\text{H}_2\text{O}$ was added to 15 mL of stock solution.

Just prior to use, the slides were removed from distilled water and dried by under a stream of nitrogen gas. For some slides, one surface was masked using a piece of Scotch Magic™ tape to limit the sol-gel coating to one side of the substrate. Slides were dipped by hand at a rate of ~1 mm/sec with no hold time and placed directly into a 20 mL scintillation vial. The vial was capped and stored on its side to minimize flow of the solution. The vial containing the sol-gel solution was capped after each dip coat (usually 2 coats) in order to minimize evaporation. The films were thermally cured in air at 70 °C for 1 to 24h, depending on the sample. A few slides were prepared using slight modifications of the above scheme. The deviations are noted in the Results section. A schematic diagram of the processing steps is shown in Figure 1.

Optical microscopy of thin films.

Polarized optical microscopy images were acquired using a Nikon Optiphot2-Pol equipped with a Sony Hyper HAD CCD-IRIS/RGB color video camera (model DXC-151A). The camera was connected to a PC using a Sony camera adapter (model CMA-

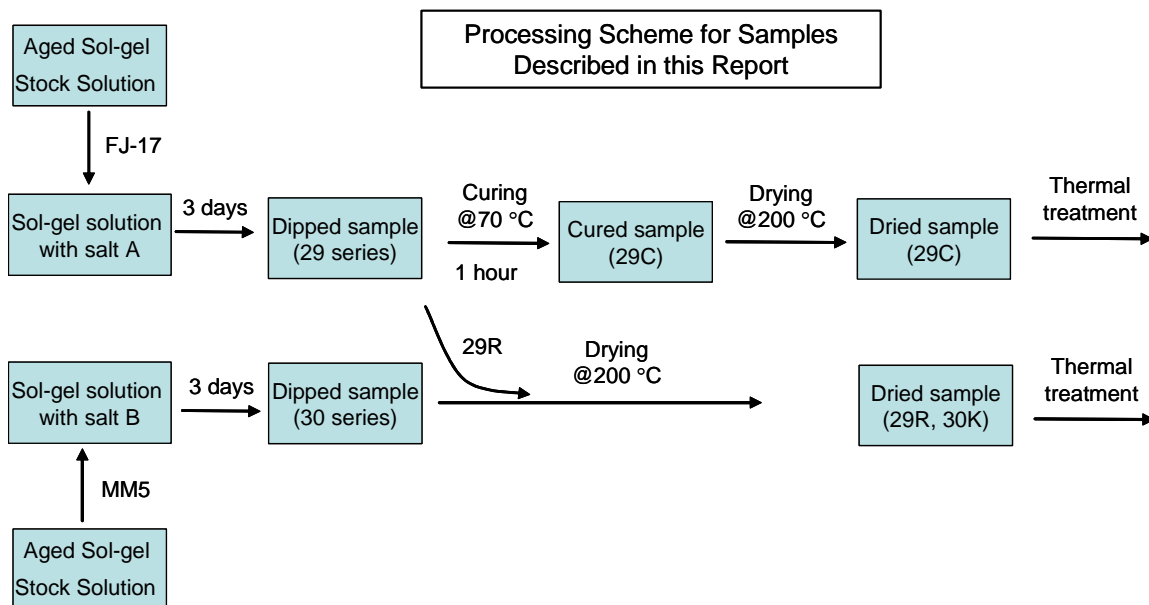


Figure 1: Schematic diagram of processing associated with key samples described in this report. Note that 29R and 30K are identical except for the source of the salt.

D2). The images were viewed using a Sony Trinitron color video monitor. Images were taken using Hauppauge computer works Win/TV software (version 2.4.17052).

Absorption spectroscopy.

Samples were prepared by weighing 2 - 3 mg of $\text{Mo}_6\text{Cl}_{12}$ in a small sample vial. The compound was then dissolved in a small amount of dry acetonitrile and transferred to a 10 mL volumetric flask. The volumetric flask was filled to the mark, stoppered, and shaken to insure a homogenous solution. Typical concentrations were 1.7×10^{-4} M. Absorption spectra were measured using a Perkin-Elmer Lambda 40 series double beam UV/vis spectrometer. Data analysis was performed using the UV Win lab (version 2.80.03) software package supplied with the instrument and plotted using Microsoft Excel. Solutions were placed into a 1 cm pathlength quartz cuvette with a separate cell containing only solvent as a reference.

Fluorescence measurements

The fluorescence measurements were performed using a Fluorolog-3 instrument from Instruments S.A., Inc. The system includes a single Czerny-Turner excitation spectrometer with a 1200g/mm ruled grating blazed at 330nm and a single Czerny-Turner emission spectrometer with a 1200g/mm holographic grating blazed at 630 nm. The excitation optics consists of a 450W ozone free Xe lamp, followed by a 270-380 nm bandpass filter (Oriel 1124). A Si photodiode is used to continuously monitor the lamp signal. The detection optics consists of 603.2 nm long wave pass filter (CVI) followed by a multi-alkali photo multiplier tube (Hamamatsu R928) with photon counting electronics. Data processing was performed using the Datamax (version 2.2) software package supplied with the instrument. Spectra were obtained by exciting at 313 nm and scanning the emission monochromator from 550 to 850 nm.

Measurements of cluster fluorescence in solution were performed by placing the solution in a quartz cuvette sealed with an airtight septum. Spectra were measured in laboratory air and high purity nitrogen (AGA, Inc, 99.999%). Prior to obtaining spectra, all gases were bubbled through the solution for 10 to 15 minutes at a rate of ~ 10 mL / min. via a glass pipette inserted through the septum. For the measurements of the potassium salts in HCl a glass pipette was used to bubble oxygen into the solution.

The measurements of the $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ emission from Mo-cluster / sol-gel composite films were made in the quartz cuvette sealed with an airtight septum. Nitrogen gas with purity 99.999% was used to obtain the luminescence spectra in a non-oxygen environment. The oxygen measurements (21% oxygen in nitrogen) were performed using 99.999% purity gas. The nitrogen and oxygen were injected bias a needle passing through the septum and allowing the gas in the cuvette to equilibrate for 10 min. An external gas flow switch was designed and built to conveniently change the gas environment without needing to touch the spectrometer compartment. This switch allows us to be completely certain that the sample does not move during repeated gas exchange.

X-ray powder diffraction.

Samples were prepared by using a spatula to evenly distribute a small amount of powdered sample on double-sided tape mounted on a microscope slide. After pressing gently to insure that the sample adhered to the tape, the microscope slide was gently tapped on its side to dislodge any loose powder.

Elemental Analysis.

The chemical composition of the $\text{Mo}_6\text{Cl}_{12}$ and $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ was determined by energy dispersive x-ray spectroscopy (EDS) using a JEOL JSM-35C scanning electron microscope (SEM) equipped with a NORAN Inc. EDS detector. The analysis was conducted at accelerating voltage 20 kV and collection time of 30s. The results of the elemental analysis for several crystals of each compound were averaged. The ratios were consistent with the formulas of $\text{Mo}_6\text{Cl}_{12}$ and $\text{K}_2\text{Mo}_6\text{Cl}_{14}$, respectively.

Thermal Analysis

Thermogravimetric analysis was performed using a Perkin Elmer TGA-7 system, which consists of a computer, TGA-7 low temperature furnace and balance module, and a TAC7/DX controller. The gas type and flow were adjusted to either nitrogen or air with a separate gas flow regulation system that was attached. The flow-rate of balance and sample gas was 45 and 40 mL/min respectively. The pan, stirrup and hanger wire were made of platinum metal that was connected to a gold balance wire using a quartz hook. Samples were normally equilibrated at 150 °C to remove residual water before analysis.

RESULTS AND DISCUSSION

Stability as defined by Thermal Gravimetric Analyses.

A requirement of optical sensors based on luminescence quenching is that the lumophore have a strong luminescence that is efficiently quenched by oxygen, and that oxygen has ready access to the lumophore. For a high temperature sensor, these characteristics must hold over the entire temperature range of interest. Since the maximum luminescence intensity of a lumophore at high temperatures is related to its intrinsic stability, a key goal for the previous quarter was to define the intrinsic thermal stability of $\text{K}_2\text{Mo}_6\text{Cl}_{14}$, the potassium salt of $\text{Mo}_6\text{Cl}_{12}$. In this work, we relied on TGA measurements of $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ coupled with parallel data from absorption and emission spectroscopy to define the upper limit of thermal stability. We ran two types of TGA measurements. In the first, we simply observed the weight loss for $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ in air as a function of temperature, with the temperature increasing at a constant rate. In addition, we carried out isothermal aging experiments where we measured the change in sample weight at a constant temperature as a function of time. These are essentially accelerated aging studies that can be used to estimate the long term stability of the clusters at lower temperatures.

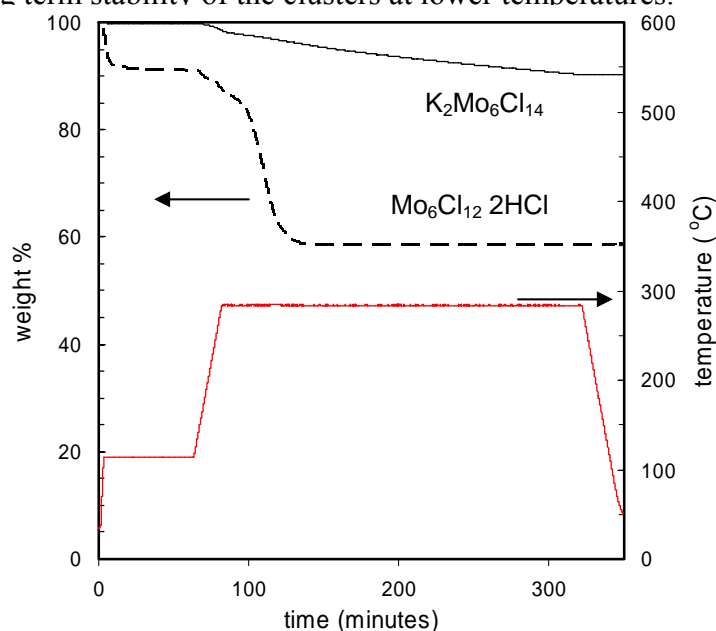


Figure 2: Thermogravimetric analysis of $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ (salt A) and $\text{Mo}_6\text{Cl}_{12} \cdot 2\text{HCl}$ showing the enhanced stability of the potassium salt relative to the hydrochloride salt. The temperature profile as a function of time for the experiment is shown at the bottom of the figure.

The TGA data shown in Figure 2 compare the thermal stability of $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ with that of the neutral cluster. The top trace in the figure shows the change in weight for the two samples as a function of time. The temperature profile shown at the bottom of the figure shows the change in temperature during the course of experiment. Initially, the samples were held at 150° for one hour to drive off residual HCl and water. The $\sim 8\%$ weight loss

at the onset of the experiment for the hydrochloride salt reflects the loss of HCl as it converts to the neutral cluster. The temperature was then ramped up to 284° C and held under isothermal conditions for four hours. In terms of thermal stability, the data show an obvious advantage for the salt compared to the neutral clusters. On reaching 280° C the neutral clusters rapidly lose weight, eventually leveling off at 58% of the original weight. In contrast the TGA data for $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ run under the same conditions show a slow weight loss that stabilizes at 90% of the original weight.

The weight-loss seen for $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ apparently corresponds to some degree of degradation. A sample of $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ was heated for two hours in air at 300° C. When removed from the TGA apparatus, the potassium salt appeared to have a dark coating on the surface. We dissolved the heat-treated sample in 6M HCl and measured its luminescence intensity. Compared to pristine samples of $\text{K}_2\text{Mo}_6\text{Cl}_{14}$, the luminescence line shape was preserved but the luminescence intensity and quenching ratio had decreased. In contrast, neutral clusters subjected to the same conditions shows no luminescence. Simply based on the TGA weight loss, we estimate that ~10% of the original material remains intact after the heat treatment.

Isothermal aging studies are consistent with this conclusion. Shown in Figure 3 are a series of TGA scans of $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ taken at various temperatures ranging from 250 to 300 °C. Initially each of the samples was heated at 150° C to drive off residual water and HCl. Time $t = 0$ (x-axis) is defined as when the sample temperature reached the target for the isothermal aging study. All scans show some weight loss and apparent degradation with the effects exacerbated at higher temperatures. The different shapes of the degradation curves preclude a simple Arrhenius-like analysis to predict lumophore lifetimes at lower temperatures, although an analysis of the early parts of the degradation process may be useful. Long-term aging studies at 250 °C are in progress.

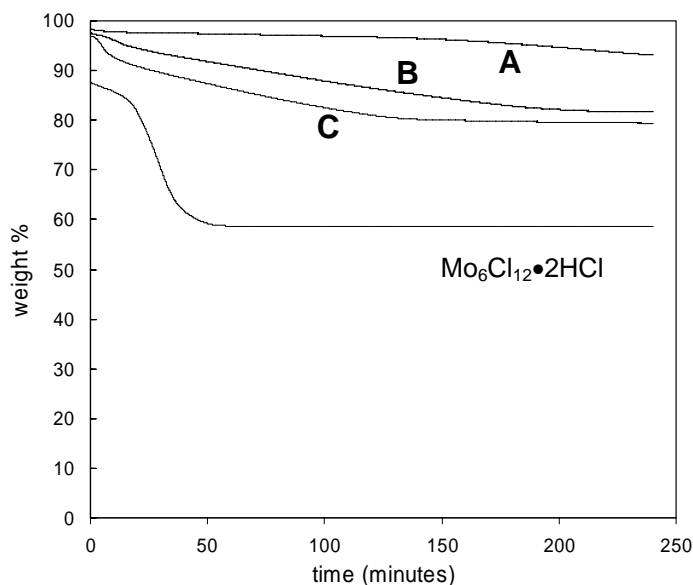


Figure 3: Isothermal aging of $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ (salt B) at 251 (A), 284 (B), and 298 °C (C). The corresponding data for $\text{Mo}_6\text{Cl}_{14}\bullet 2\text{HCl}$ aged at 250°C is shown for comparison.

Overall, TGA experiments confirm that the potassium salt is more thermally stable than the neutral cluster, but the experiments also suggest that continuous applications of $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ are likely to be limited to $<300^\circ\text{C}$. However, short-term high-temperature excursions could be tolerated.

High temperature survivability of $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ /sol-gel films.

We also carried out combined optical and thermal experiments where the salt has been embedded in sol-gel matrices on quartz substrates. Numerous potassium-salt/sol-gel film slides were dipped and then subjected to a variety of thermal processes, in terms of both temperature and time, to determine the survivability of the luminescence from the films following high temperature processing. The properties of three samples are described in detail in this report, 29C, 29R, and 30K. 29C is representative of the majority of coated slides prepared to date in that it was cured at 70°C (see Figure 1). Slides 29R and 30K represent a shift in our sol-gel process that is designed to introduce higher porosity in the films.

We use measurements of the luminescence spectra of film 29C in flowing nitrogen as an indicator of the survivability of the sol-gel film after temperature cycling. The use of a single slide for these experiments minimizes ambiguities associated with slide the slide variation. The film was dipped coated three times in a 9-day old Mo-cluster/sol gel solution, made from potassium salt A. Following drying under ambient conditions for 20 days it was cured at 70°C for 24 hours. Shown in **Figure 4** are the normalized (with

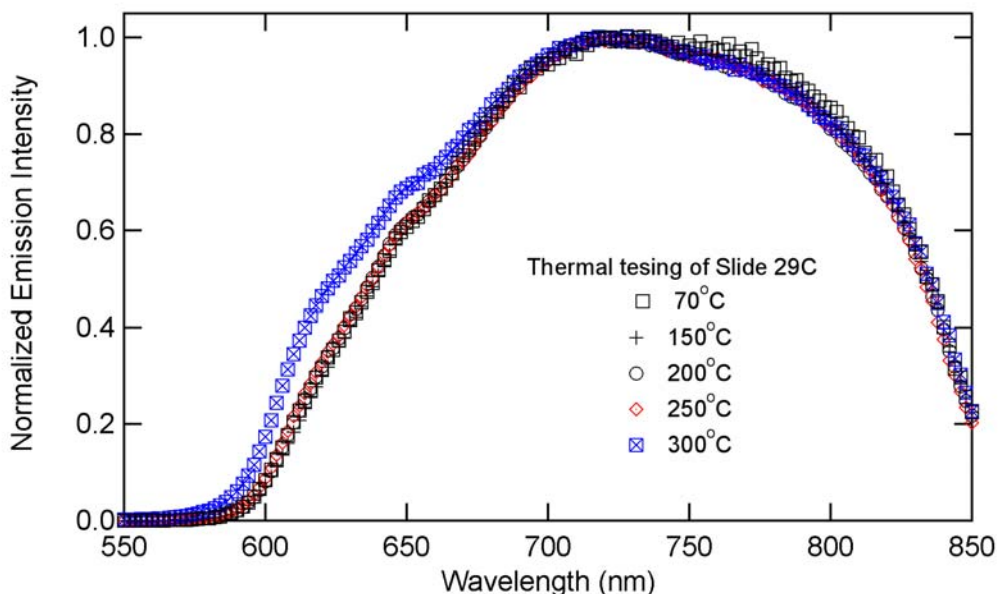


Figure 4: Luminescence spectra of the $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ sol-gel film 29C (salt A) following thermal cycling. Shown are the emission spectra of the film following () 1 day cure @ 70°C , (+) 2 hour anneal at 150°C , (○) 1 hour anneal @ 200°C , (◇) 1 hour annealed at 250°C and (□) 1 hour at 300°C . The spectra are all normalized with the maximum @ $725 \pm 5\text{ nm}$ to present the evolution of the line-shapes with temperature. All measurements are taken in 99.999% nitrogen.

respect to the peak intensity at 725 ± 5 nm) emission spectra of the film in pure nitrogen. The film was subsequently annealed at 150 °C for 2 hours, 200 °C for one hour, 250 °C for one hour, and 300 °C for one hour and the emission spectra was measured after each annealing step. For temperatures up to 250 °C there is no change in the line shape, a slight broadening of the line is observed after heating at 300 °C. **Figure 5** shows the normalized emission intensity in nitrogen and the quenching ratio (pure N₂ / 21% O₂) of the same film. Note that the absolute luminescence intensity remains approximately constant in the 150 to 250 °C range. These data indicate that the photophysics of the cluster is not adversely affected by hour-long excursions to 250 °C, however cycling to 300 °C for one hour does begin to change the cluster.

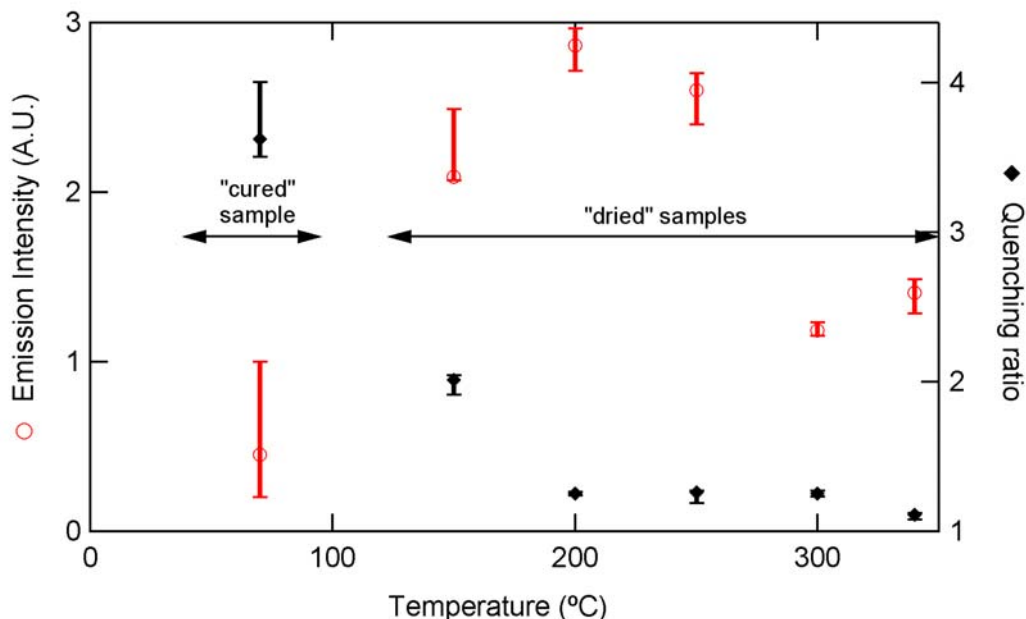


Figure 5: Normalized emission intensity in nitrogen and quenching ratio (pure N₂ / 21% O₂) for the K₂Mo₆Cl₁₄ sol-gel film 29C (salt A) following thermal cycling. Measurements were made following a 1 day cure at 70°C, a 2 hour anneal at 150°C, a 1 hour anneal at 200°C, a 1 hour anneal at 250°C, a 1 hour anneal at 300°C and a 1 hour anneal at 340°C. The spectra are all normalized with the maximum at 725 ± 5 nm. The quenching ratio is the ratio of the luminescence intensity in 99.999% N₂ to that in 21% O₂. The data demonstrated the cluster luminescence survives to ~300°C.

Matrix effects on quenching.

A critical design issue is the matrix used to embed the lumophore, which must have high oxygen permeability to achieve near real-time oxygen sensing. We attribute the reduction of the quenching ratio for 29C and similar films to densification of the sol-gel matrix, which reduces the permeability of the film. The permeability of sol-gel matrices is related to the free volume within the matrix and is highly dependent on the details of the synthetic parameters used to prepare the sol-gel matrix cell gel. Briefly, a sol-gel synthesis involves the acid or base catalyzed hydrolysis and condensation of metal alkoxides such as tetraethylorthosilicate (TEOS). As the reaction proceeds to completion

the sol-gel solution is converted to a continuous solid matrix. If spectator compounds are present, in our case $\text{K}_2\text{Mo}_6\text{Cl}_{14}$, they are entrapped within the matrix. Essentially all sol-gel films densify to some extent as they cure and further densify after drying at high temperatures. However, the porosity of the final matrix can be altered by the addition of a diluent or by adjusting the processing conditions used to cure and dry the matrix. For example, added solvent reduces the concentration of TEOS and favors the formation of individual silica particles in the sol-gel solution. Films cast from such a solution will tend to be locally heterogeneous and have a high free volume. In contrast, casting a sol-gel solution before substantial particle formation has taken place leads to a more uniform film, but with a higher density and lower permeability.

Another stability issue is the chemical compatibility of the sol-gel chemistry with the lumophore. Previous data show that $\text{Mo}_6\text{Cl}_{12}$ is unstable in alcohol solvents at temperatures $>70^\circ\text{C}$. The relevant chemistry is believed to be the formation of molybdenum oxo species, a first step in the degradation of the Mo_6Cl_8 core. The classical recipes for sol-gel syntheses call for curing films at an intermediate temperature ($50\text{--}70^\circ\text{C}$) followed by drying at a higher temperature (200°C) to drive off residual water and solvent from the film. Thus the combination of heat and alcohol (from hydrolysis of TEOS) can potentially degrade $\text{Mo}_6\text{Cl}_{12}$ and to a lesser extent $\text{K}_2\text{Mo}_6\text{Cl}_{14}$.

Our working hypothesis is that long curing times allows the sol-gel film to evolve into a homogeneous matrix with low permeability. Eliminating curing and going straight to drying at 200°C should enable removal of solvent and water without appreciable degradation of the lumophore. In addition, rapid curing/drying should lead to a more porous matrix since heterogeneity in the sol-gel film would be preserved. We believe that densification of the sol-gel matrix is responsible for the reduction in the quenching ratio seen for sample 29C after the sample was dried above 150°C . After curing at 70°C , the quenching ratio was ~ 3.5 , compared to <10 for liquid samples. Drying further decreased the permeability, and the ratio fell to <2 . To test this idea, we prepared a $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ /sol-gel film (29R) from salt A and directly dried the film at 200°C , bypassing the 70°C cure. The luminescence spectra of this film in pure nitrogen and 21 % oxygen are shown in **Figure 6**. The results are very encouraging. In terms of absolute counts the luminescence from the film is high and the quenching ratio is $\sim 4\text{X}$. To demonstrate the repeatability of our new sol-gel film processing technique, another slide (30K) was made using the same processing as 29C, but using an independently synthesized salt, salt B in this case. As shown in **Table 1**, the normalized intensity in nitrogen for slide 30K and 29C are essentially equivalent, and a quenching ratio of 3.4X was measured for slide 30K. We are in the process of determining the maximum time / temperature exposure for the potassium salt sol-gel films. Our results demonstrate that we have identified a synthetic route to form $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ /sol-gel films that can survive continuous operation for at least 60 minutes at 200°C with quenching ratios that are adequate for fiber sensor development. Excursions up to 300°C are also possible, for shorter periods of time.

In a parallel experiment, the potassium salt / sol-gel composite has been deposited on UV transparent fibers. We are in the process of testing the thermal and mechanical properties of these composites

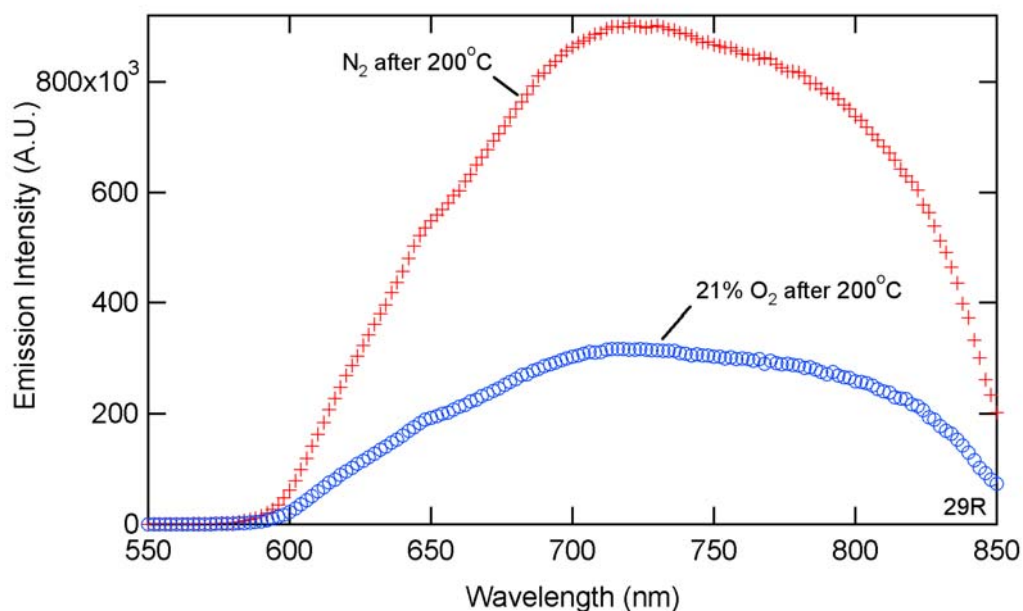


Figure 6: Luminescence spectra of $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ / sol-gel film 29R (salt A) directly cured at 200 °C for 30 minutes. Quenching of 4.1X is observed between 99.999% pure nitrogen and 21% oxygen in nitrogen.

Sample	Temperature cycle	Normalized intensity in N_2	Quenching Ratio (pure N_2 / 21% O_2)
29C (Salt A)	70°C 24 hr	0.45	3.7
	150°C 2 hr	2.1	2.0
	200°C 1 hr	2.9	1.2
	250°C 1 hr	2.6	1.3
	300°C 1 hr	1.2	1.2
	340°C 1 hr	1.4	1.1
29R (Salt A)	200°C 0.5 hr	2.3	4.1
	200°C 1 hr	2.6	2.5
30K (Salt B)	200°C 0.5 hr	2.0	3.4

Table 1: Luminescence measurements following thermal cycling for three potassium salt / sol-gel films. The data demonstrates that the films can survive temperature cycling to 300 °C, quenching by oxygen of up to 4X was observed following heating to 200 °C.

CONCLUSIONS

TGA experiments confirm that superior thermal stability of $K_2Mo_6Cl_{14}$ compared to Mo_6Cl_{12} . They experiments also suggest that continuous applications of $K_2Mo_6Cl_{14}$ are likely for temperature $<250^\circ C$, with some tolerance for short-term high-temperature excursions. We also have defined the experimental parameters that lead to thermally robust $K_2Mo_6Cl_{14}$ / sol-gel films. From two independent runs we have demonstrated that quenching between 99.999% N_2 and 21% O_2 of a factor of four can be obtained following thermal cycling of half an hour at $200^\circ C$. Both the quenching ratio and the number of photons available are promising for development of a high temperature fiber sensor. Experiments are underway to corroborate these results with *in-situ* measurements of the luminescence and quenching ratio as a function of temperature. In addition we are investigating the upper bound in terms of both temperature and time on the thermal stress cycle of these potassium salt / sol-gel films.

REFERENCES

- [1] R. D. Mussell, Ph. D. thesis, Michigan State University (East Lansing), **1988**.
- [2] M. D. Newsham, Michigan State University (East Lansing), **1988**.
- [3] M. D. Newsham, M. K. Cerreta, K. A. Berglund, D. G. Nocera, *Mater. Res. Soc. Symp. Proc.* **1988**, 121, 627.
- [4] C. J. Ruud, Ph. D. thesis, Michigan State University (East Lansing), **1999**.
- [5] R. N. Ghosh, G. L. Baker, C. Ruud, D. G. Nocera, *Appl. Phys. Lett.* **1999**, 75, 2885.
- [6] J. T. Remillard, J. R. Jones, B. D. Poindexter, C. K. Narula, W. H. Weber, *Appl. Opt.* **1999**, 38, 5306.
- [7] J. C. Sheldon, *J. Chem. Soc.* **1960**, 1007.
- [8] L. M. Robinson, H. Lu, J. T. Hupp, D. F. Shriver, *Chemistry of Materials* **1995**, 7, 43.

BIBLIOGRAPHY

None.

LIST OF ACRONYMS AND ABBREVIATIONS

Moly Oil – $Mo_6Cl_{12} \cdot 2CH_3CN$ in acetonitrile

HCl – Hydrochloric Acid

MeOH – Methanol

CH_3CN – Acetonitrile

TEOS – Tetraethyl orthosilicate

APPENDIX A - ACKNOWLEDGEMENTS

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