

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. The luminescence of $\text{Mo}_6\text{Cl}_{12}$ immobilized in a sol-gel matrix was measured as a function of heater temperature up to 200 °C, in an inert environment. While the luminescence decreased with temperature, the integrated intensity at 200 °C should be sufficient to enable detection of the luminescence in a fiber geometry. Previously we found that aging $\text{Mo}_6\text{Cl}_{12}$ at temperatures above 250 °C converts the canary yellow $\text{Mo}_6\text{Cl}_{12}$ to a non-luminescent gray solid. Optical and thermal aging experiments show that the alkali metal salts of $\text{Mo}_6\text{Cl}_{12}$ have higher thermal stabilities and remain luminescent after aging at 280 °C.

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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. [1,2,3] 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 [4] 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 [5]. With these facts in hand, we anticipate promising results from our design.

EXECUTIVE SUMMARY

Previously, we successfully immobilized $\text{Mo}_6\text{Cl}_{12}$ in a porous sol-gel film, thus accomplishing a critical step towards the development of an inorganic fiber optic oxygen sensor for high temperature applications. High temperature stability issues were addressed by characterizing the optical properties of thin sol-gel films deposited on planar fused silica substrates. Quenching of the red luminescence was observed in the Mo-cluster/sol-gel composite films deposited on a quartz substrate following temperature cycling to 200°C. The emission line shape is unchanged from that of $\text{Mo}_6\text{Cl}_{12}$ in solution, which indicates that the cluster photophysics is not adversely affected by incorporation into the sol-gel matrix or by heating to 200 °C. The composite film has the mechanical properties required for a harsh environment fiber sensor, as demonstrated by the strong adhesion of the thin films to the quartz substrate. We anticipate that the sol-gel process developed for planar silica substrates will be transferable to high temperature UV-visible silica optical fibers.

We measured the luminescence of immobilized clusters as a function of heater temperature in an inert environment up to 200°C. Measurements of the degree of oxygen quenching are in progress. We see a general decrease in luminescence with increases in temperature. Based on our previous experience with fiber optic oxygen sensors [4], the integrated intensity of the signal at elevated temperature should be sufficient to use in a fiber optic geometry. A preliminary study of the high temperature stability of the $\text{Mo}_6\text{Cl}_{12}$ clusters in oxygenated environments revealed irreversible changes in the optical absorption spectrum at >250 °C and a loss of the red luminescence that is characteristic of pristine clusters. Thermal aging experiments run in air and under nitrogen point to oxidation of the clusters as the cause of the change in optical properties. We synthesized the potassium salt of $\text{Mo}_6\text{Cl}_{12}$ ($\text{K}_2\text{Mo}_6\text{Cl}_{14}$) and found that the alkali salts of $\text{Mo}_6\text{Cl}_{12}$ are more stable than the parent compound. Optical and thermal aging experiments show that the alkali metal salts of $\text{Mo}_6\text{Cl}_{12}$ have higher thermal stabilities and remain luminescent after aging at 280 °C.

EXPERIMENTAL

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

MoCl_2 from City Chemical (lot 30L114) 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 (CCI, electronics grade) were added to 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 speed filter paper to remove insoluble white and metallic particles. The filtered solution was heated on a hot plate and the volume was reduced to 200 mL. 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, yellow needles were collected by gravity filtration and spread out on several pieces of filter paper to dry under ambient conditions for two days. Yield: 586 mg. A second crop was obtained by concentration of the mother liquor to 100 mL by heating, filtration followed by a further a reduction in the 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, and fluorescence spectroscopy.

Preparation of the acetonitrile complex of $\text{Mo}_6\text{Cl}_{12}$. ($\text{Mo}_6\text{Cl}_{12}\cdot 2\text{CH}_3\text{CN}$)

All glassware and solvents were dried prior to use. The $\text{Mo}_6\text{Cl}_{12}$ hydrochloride salt was heated under vacuum at 210 °C for 12 hours to yield $\text{Mo}_6\text{Cl}_{12}$. The resulting yellow powder was loaded into the thimble of a pre-dried Soxhlet extraction apparatus. Dry acetonitrile (250 mL) was added to the extractor and the receiving flask was heated to start the extraction process. After 3 days, the yellow solution was removed and concentrated to 10 mL. The products were characterized using, uv-vis, and fluorescence spectroscopy. $\text{Mo}_6\text{Cl}_{12}\cdot 2\text{CH}_3\text{CN}$ was also directly prepared from MoCl_2 from City Chemical (lot40C65,) using the same procedure.

Preparation of the potassium salt of $\text{Mo}_6\text{Cl}_{12}$. ($\text{K}_2\text{Mo}_6\text{Cl}_{14}\cdot 2\text{H}_2\text{O}$) (3)

KCl (5 mL of a solution prepared by dissolving KCl (1.0077g, 13.5 mmol) in 50 mL of 6M HCl) was added to a stirred solution of $\text{Mo}_6\text{Cl}_{12}$ (25 mL, 2.05×10^{-3} M) in 6M HCl in an Erlenmeyer flask. The resulting yellow solution was concentrated to 15 mL by boiling on a hot plate with stirring. The solution was slowly cooled to room temperature on the hot plate and then 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 placed onto several pieces of filter paper and allowed to dry under ambient conditions, to give 28.4 mg of bright yellow crystals.

Preparation of sol-gel films.

A typical sol-gel process is described below. To an 10 mL Erlenmeyer flask containing a stirred solution of tetraethyl orthosilicate (2.0 mL) and $\text{Mo}_6\text{Cl}_{12}\cdot 2\text{CH}_3\text{CN}$ (g in 1.4 mL

acetonitrile) was added 0.65 mL of 1M HCl. After stirring for 1 hr, the stir bar was removed and the solution was aged for 2 hrs at 70 °C in a hot oil bath. Following aging, the solution was poured into a 20 mL screw cap scintillation vial, and tightly capped to minimize evaporation. The overall composition of the solution was H₂O/tetraethyl orthosilicate = 4, solvent/tetraethyl orthosilicate = 3.

Sol gel films were deposited on glass or quartz slides. Slides were handled while wearing Supreno SE™ brand powder free nitrile gloves. The slides were washed with Alconox™, rinsed with distilled water, and soaked in a base bath for ~6 hours. Just prior to use, the slides were rinsed with distilled water and soaked in distilled water. Each slide was dried using a stream of house nitrogen and immediately coated by dipping the slide into the sol-gel solution at a rate of approximately one mm/s. 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. The sol gel solution vial was re-capped after each dip coat. The coated slides were either (1) placed flat on a piece of aluminum foil and the aluminum foil and placed into an oven at 70 °C for 24 hours to cure or (2) placed in a capped 20 mL vial laying on its side. The evaporation rate was controlled by how tightly the vial was sealed. Slow evaporation rates gave films with better adhesion and fewer cracks. When dry, the vial and slide (no cap) were placed in an oven at 70 °C for a period of 24 hours to cure. The tape was then removed using a razor blade, and any remaining glue was removed with acetone.

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.

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.

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 or 436 nm and scanning the emission monochromatic from 500 to 1000 nm, or 550 to 850 nm.

Measurements of the cluster fluorescence in different concentrations of gaseous oxygen were performed by placing the quartz slide with the cluster /sol-gel composite in a quartz cuvette sealed with an airtight septum. Nitrogen gas of purity 99.999% was used to obtain the measurements in a 0.001% oxygen environment. The atmospheric measurements (~20% oxygen) were performed after removing the septum, and allowing the gas in the cuvette to equilibrate for 30 min.

The measurements of the $\text{Mo}_6\text{Cl}_{12}$ emission from Mo-cluster / sol-gel composite films, as a function of temperature were made in the same quartz cuvette described above. A platinum microheater (part 32 208 172 from Heraeus Sensor Technology) was attached with a thermally conducting silver print (GC 22-202 from GC Electronics) to the backside of the quartz slide. The silver print is allowed to cure for at least one hour in air at 100. °C. Electrical connection to the Pt heater was made by microwelding 5 mill thick Cu wire to the 5 mill thick legs of the Pt microheater. The electrical leads were then threaded through the septum. The microheater was powered with a regulated voltage supply. We determined the heater temperature by monitoring the heater resistance, and using the resistance versus temperature curves for a standard 100 ohm Pt thermometer. Prior to the experiments in the SPEX fluorimeter, a curve of temperature as a function of heater power was obtained with the same gas flow as that was used during the actual experiments. We estimate that the temperature of the Mo-cluster / sol-gel film, on the other side of the 1mm thick quartz slide, is at most 30 °C lower than the heater temperature. This will be determined more accurately by attaching a solid state 100 ohm Pt thermometer on top of the film itself, and measuring the sample temperature under the same conditions as that of the emission measurements.

Absorption spectroscopy

The samples were prepared by weighing 8 – 8.5 mg of $\text{Mo}_6\text{Cl}_{12}$ in a small sample vial. The compound was then dissolved in a small amount of aqueous 6 M HCl and transferred to a volumetric flask. The volumetric flask was filled to the mark, stoppered, and shaken to insure a homogenous solution. Concentration: 1.7×10^{-4} M. Absorption measurements were performed using a Perkin Elmer Lambda 40 Double beam instrument. The data was acquired using UV Winlab software version 2.8 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.

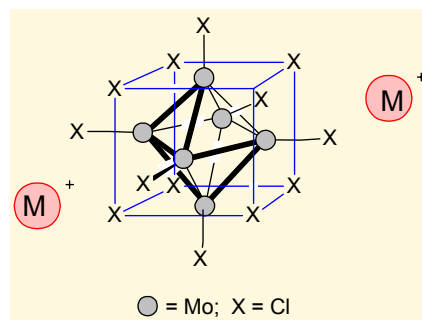
Time resolved fiber sensor test setup

We have begun designing the time resolved sensor test set up to measure the response of the fiber sensors with millisecond resolution. The fiber sensor will be held stationary in a fixed mount. Located 1 mm above the sensor will be a moving gas head with two gas outlets (gas A and gas B) of ~1 mm in size. The moving gas head will be mounted on an electrostatic actuator (Densitron, DRTL32). The actuation will translate the gas outlets by about 2 mm in 1 ms and switch the gas at the sensor from A to B.

RESULTS AND DISCUSSION

Evaluation of alkali metal salts of $\text{Mo}_6\text{Cl}_{12}$ for improved thermal stability.

As the synthesis of $\text{Mo}_6\text{Cl}_{12}$ is carried out at $T > 600^\circ\text{C}$, the inherent thermal stability of $\text{Mo}_6\text{Cl}_{12}$ is high. However, earlier we showed that in oxygenated environments the canary yellow clusters undergo oxidation at $T > 250^\circ$ to form a gray solid that does not luminesce. Elemental analysis indicates a chemical composition of MoO_x , consistent with oxygenation. Two open axial coordination sites on the $\text{Mo}_6\text{Cl}_{12}$ cluster lead to the polymerization of clusters through shared chlorine bridges. These open sites also are the likely source of the oxidative instability of $\text{Mo}_6\text{Cl}_{12}$. The known $\text{Mo}_6\text{Cl}_{14}\text{X}_2$ salts, where X is an alkali metal cation such as Na^+ , K^+ , or Cs^+ should be more thermally robust since there is a full complement of chloride ligands and no open sites for cluster aggregation or oxidation, i.e. chlorides must be lost from the cluster for the cluster to undergo degradation. [6]



The potassium salt of $\text{Mo}_6\text{Cl}_{12}$ ($M=\text{K}$)

We initially synthesized the K^+ salt via a high temperature (800°) metathesis reaction. In addition to being cumbersome, the product contained substantial amount of impurities. On the advice of Prof Maverick at Louisiana State University, we switched to a simple

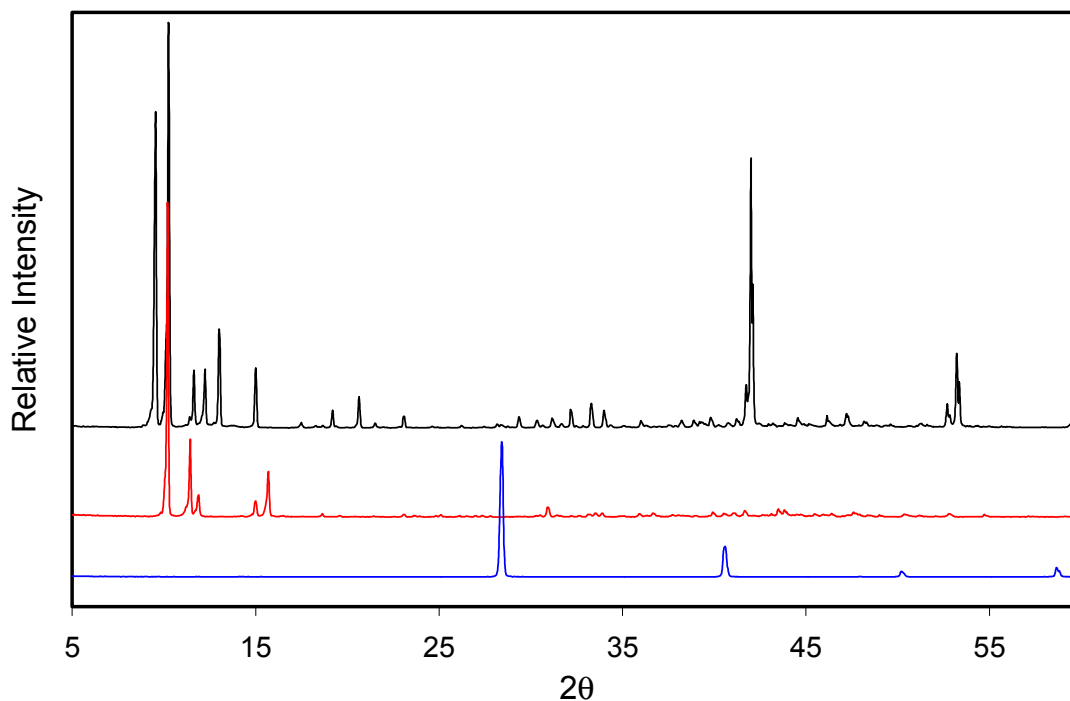


Figure 1. Powder x-ray diffraction patterns for (top) $\text{Mo}_6\text{Cl}_{12}$, (middle) $\text{K}_2\text{Mo}_6\text{Cl}_{14}\cdot 2\text{H}_2\text{O}$, and (bottom) KCl .

solution-based synthesis. $\text{Mo}_6\text{Cl}_{12}$ dissolved in HCl and treated with a large excess of KCl. The $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ complex precipitated from solution and was collected by filtration. The K^+ salt was characterized by powder x-ray diffraction, uv-vis, and fluorescence spectroscopy. As shown in **Figure 1**, the powder x-ray diffraction pattern shows the transformation of the hydrochloride salt to the more stable potassium salt. The optical data also are consistent with successful synthesis of the salt, but the similarity of the optical properties of $\text{Mo}_6\text{Cl}_{12}$ and the K^+ salt makes it difficult to conclude that there was no contamination by $\text{Mo}_6\text{Cl}_{12}$. Elemental analysis will be used to assay the K/Cl and K/Mo ratios in the materials and quantify cluster purity.

Thermal analysis of the resulting complex shows improved thermal stability compared to $\text{Mo}_6\text{Cl}_{12}$. TGA measurements run in air at $10^\circ/\text{min}$ (**Figure 2**) showed reduced weight losses, and more importantly, after 2 hours at 280°C the samples still luminesced. $\text{Mo}_6\text{Cl}_{12}$ run under the same conditions were optically dead. The color of the salt complex evolved from yellow to a greenish hue. For reasons noted above, we are unsure whether the color change resulted from partial degradation of the cluster, or is due to contamination by $\text{Mo}_6\text{Cl}_{12}$.

$\text{Mo}_6\text{Cl}_{12}$ and its potassium salt, $\text{K}_2\text{Mo}_6\text{Cl}_{14}\cdot 2\text{H}_2\text{O}$, were heated to 280°C in air for 1 hour, and after cooling to room temperature, both were dissolved in 6M HCl. The uv-vis spectra of the resulting solutions were measured. The data of **Figure 3** clearly show the

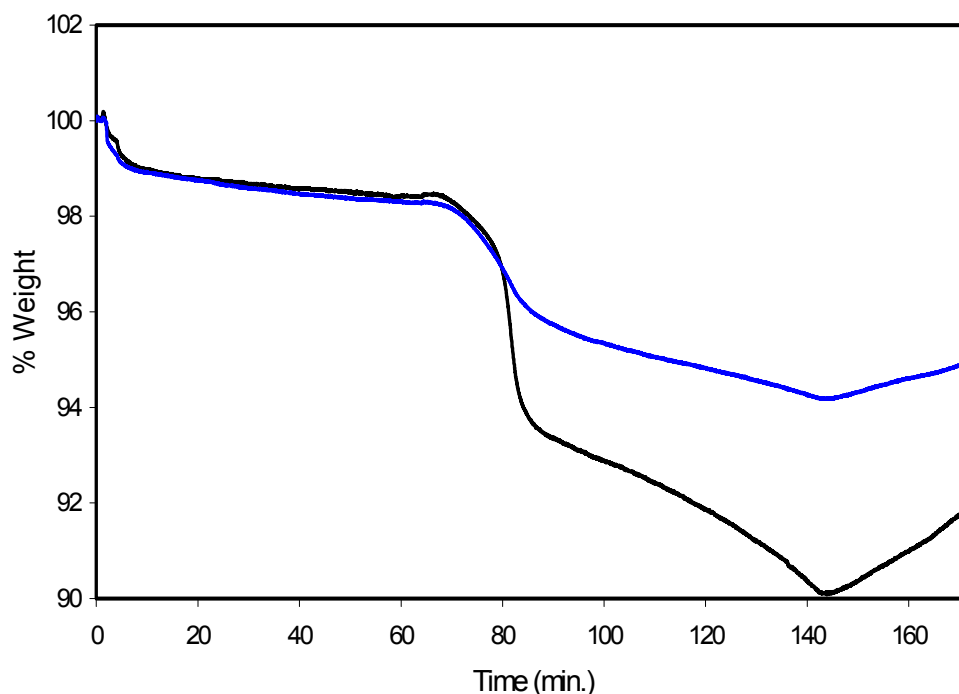


Figure 2. Thermal Gravimetric Analysis in air of (—) $\text{Mo}_6\text{Cl}_{12}$ and (—) $\text{K}_2\text{Mo}_6\text{Cl}_{14}$. The samples were (1) heated to 120°C at $30^\circ/\text{min}$, (2) held at 120° for 1 h, (3) heated to 280°C at $10^\circ/\text{min}$, (4) held at 280°C for 1 hour, and (5) cooled to 40°C at $10^\circ/\text{min}$.

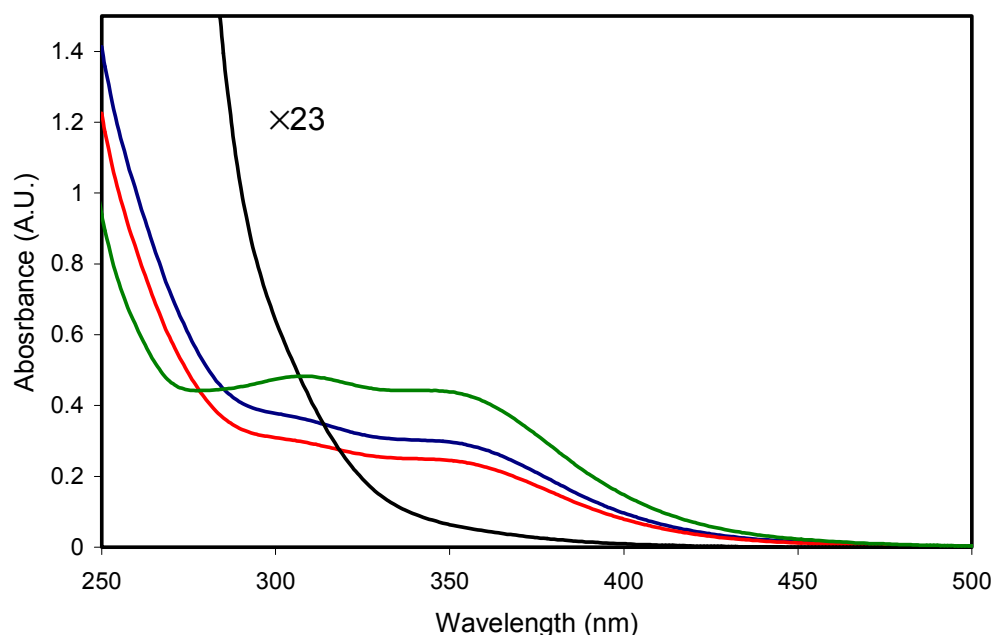


Figure 3. Absorption spectra for cluster samples heated at 280 °C for 60 minutes and then dissolved in 6M HCl. Samples shown are (—) $\text{K}_2\text{Mo}_6\text{Cl}_{14}$, heated in air in the TGA apparatus and (—) in a microscope hot stage, (—) $\text{Mo}_6\text{Cl}_{12}$ heated in a hot stage, and (—) unheated $\text{Mo}_6\text{Cl}_{12}$. The concentrations of each solutions were 0.17g/L, except for the heated $\text{Mo}_6\text{Cl}_{12}$ sample, which was 23 times higher (4g/L).

enhanced thermal stability of the potassium salt. The intensity of the $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ spectrum is $\sim 2/3$ of that for unheated $\text{Mo}_6\text{Cl}_{12}$ while that for heat treated $\text{Mo}_6\text{Cl}_{12}$ (run at a 23 \times higher concentration) shows none of the characteristics of the original complex.

Immobilization $\text{Mo}_6\text{Cl}_{12}$ clusters in sol-gel films.

We have developed a process to immobilize the clusters in inorganic sol-gel matrices. In this synthesis we combined tetraethyl orthosilicate (TEOS), acetonitrile, a catalytic amount of HCl, and a solution of the $\text{Mo}_6\text{Cl}_{12}$ cluster in the form of its acetonitrile complex ($\text{Mo}_6\text{Cl}_{12} \cdot (\text{CH}_3\text{CN})_2$). The latter was conveniently prepared by placing $\text{Mo}_6\text{Cl}_{12}$ clusters in a soxhlet extractor charged with dry acetonitrile and continuously forming and extracting the soluble complex from the insoluble yellow $\text{Mo}_6\text{Cl}_{12}$ clusters. Typically, the concentration of clusters in the acetonitrile solution used in the sol gel process was $\sim 10 \text{ mg/mL}$ ($9.2 \times 10^{-3} \text{ M}$). After combining the reactants and heating to 70 °C for 1 hour (aging), the solution was dip or spin-coated onto substrates. The sol gel films showed excellent adhesion to substrates terminated in silanol groups (glass, quartz, silicon, ...), providing the substrates were fully cleaned. A protocol similar to that used in semiconductor processing (base bath, followed by rinsing and storage in high purity water) ensured a clean surface for film deposition. This procedure is fully compatible with high temperature optical fiber probes.

We explored the viscosity/thickness relationships for sol/gel deposition to determine the minimal time needed for the aging and curing steps in the sol/gel process. While higher temperatures accelerate aging, accelerating the curing process must be approached with caution. The curing period begins at the time that a substrate is coated with the sol gel solution and lasts until the samples are dried in an oven to complete the curing of the film. During this time, the hydrolysis of ethoxysilane groups (Si-OEt) is nearly completed and the Si-O-Si network structure developed. Typical curing processes for sol gel processes can be as long as weeks at room temperature, and we sought to decrease that time by curing at elevated temperatures. We found that the immobilized $\text{Mo}_6\text{Cl}_{12}$ clusters reacted chemically, presumably with residual ethanol from the hydrolysis process, to form non-luminescent complexes. This is consistent with prior work that described $\text{Mo}_6\text{Cl}_{12}$ as being somewhat sensitive to substitution by oxygenated species in basic environments.[7] We view this as a minor limitation; since simply curing films for longer times at room temperature leads to clear, high quality luminescent films.

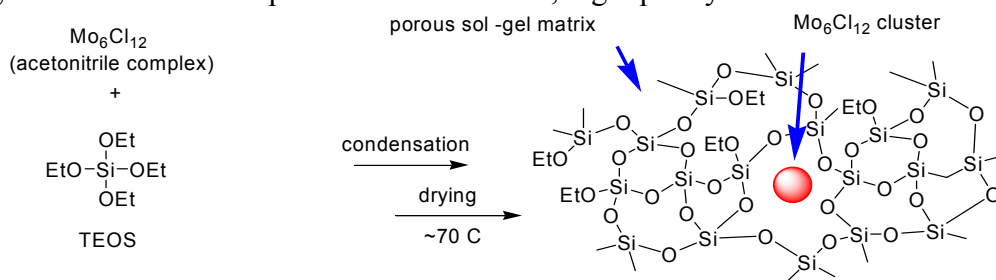


Figure 4. Synthetic route to immobilized molybdenum clusters.

Oxygen quenching of sol-gel films containing $\text{Mo}_6\text{Cl}_{12}$

Oxygen quenching of the luminescence from the Mo-cluster/sol gel film 15F after heating to 200°C are shown in **Figure 5**. The film was heated to 200°C for one hour prior to the measurement. Note that the clusters immobilized in the sol-gel matrix after heat treatment have the same emission lineshape as the isolated clusters in solution, which indicates that neither the sol-gel chemistry nor heating to 200°C have adverse effects on the cluster photophysics. We believe that the lower degree of oxygen quenching in the sol-gel matrix as compared to the solution results is related to the porosity of the sol-gel matrix, which can be controlled by aging time and the inclusion of porogens in the sol-gel process.

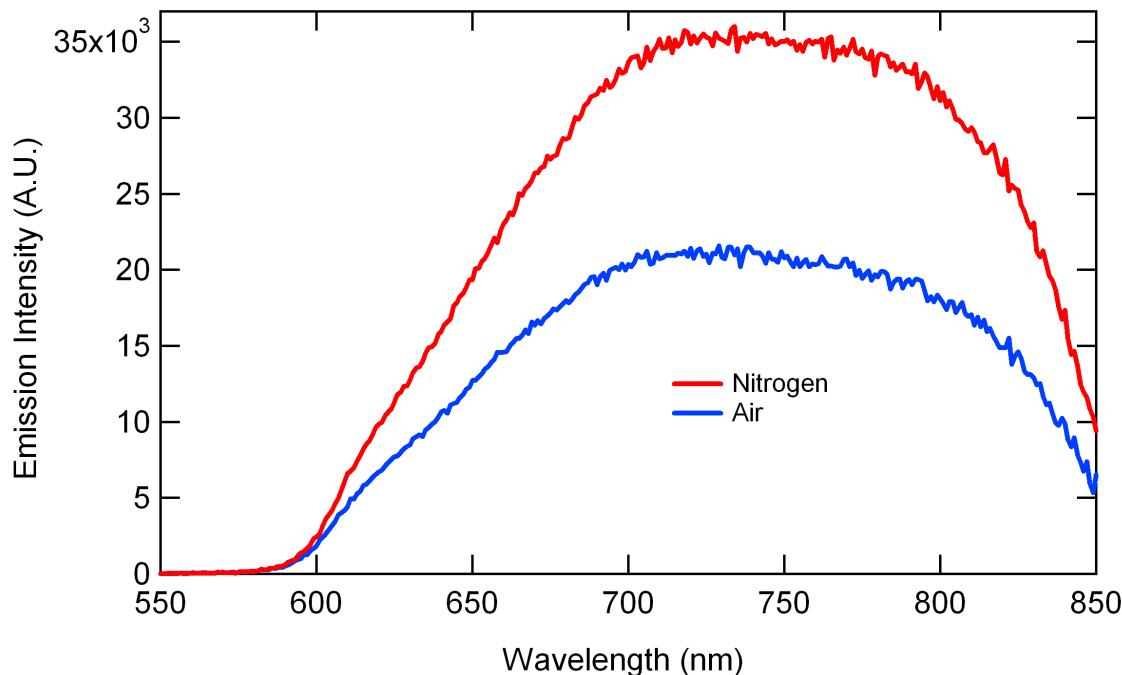


Figure 5. Emission spectra of Mo-cluster / sol-gel composite film 15F, after heating to 200 °C for one hour. Quenching of 1.7X is observed between nitrogen (<0.001% oxygen) and air (~20% oxygen). Excitation wavelength is 313 nm.

Measurement of $\text{Mo}_6\text{Cl}_{12}$ luminescence as a function of temperature.

The luminescence of sol-gel film 15F was measured as a function of temperature in flowing N_2 (purity 99.999%). Shown in **Figure 6** is the integrated signal intensity (i.e. integrating all the luminescent photons in the 580-850 nm emission bandwidth of Fig. 5) of the sample as a function of heater temperature. The luminescence signal decreases with increasing temperature, as observed previously in the 1.4 to 300 K regime [8]. No temperature dependent hysteresis was observed as the measurements were taken in the following order: 22 °C, 49 °C, 103 °C, 163 °C, 200 °C, 137 °C, 85 °C, 41.5 °C, 189 °C, and 31.5 °C. Note that the temperature scale in **Figure 6** is that of the platinum heater glued to the back of the quartz substrate. We estimate that the temperature of the Mo-cluster / sol-gel film itself is a most 30 °C lower than the heater temperature. Experiments are currently under way to measure the sol-gel film temperature as a function of heater power using a 100 ohm Pt solid state thermometer. Measurements of the degree of oxygen quenching as a function of temperature are in progress.

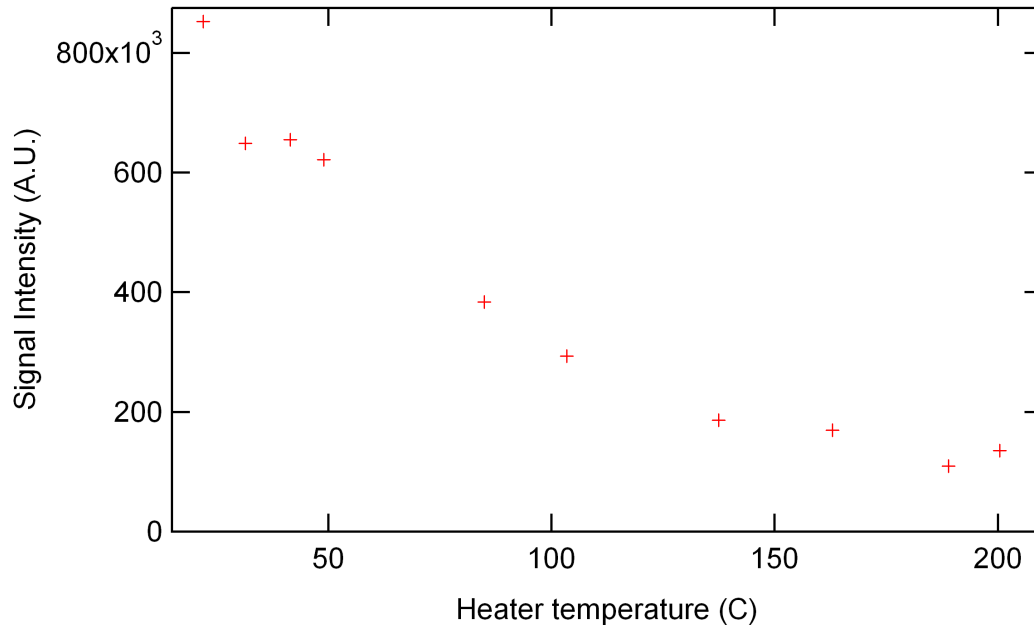


Figure 6. Integrated luminescence intensity (580 - 850 nm) of Mo-cluster / sol-gel composite film 15F as a function of heater temperature. The measurements were taken in flowing nitrogen (99.999%).

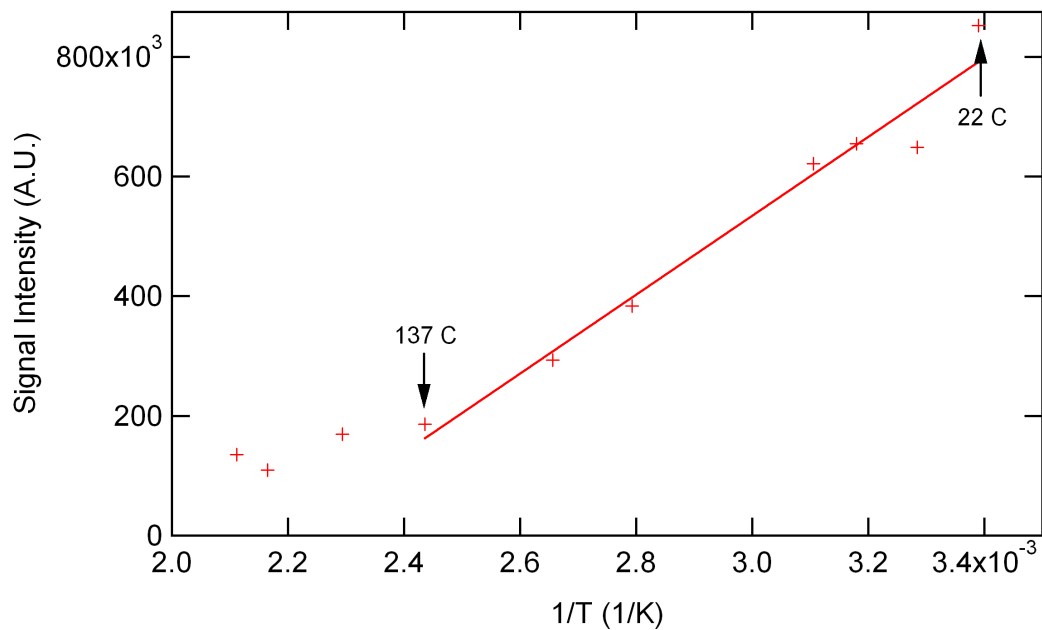


Figure 7. Data from Figure 6 plotted as a function of inverse temperature.

Figure 7 shows the data from **Figure 6** plotted as a function of inverse temperature. Preliminary analysis of our data indicates that from room temperature to about 410 K (137 °C) we have a $1/T$ temperature dependence. Above 140 °C, another mechanism appears to become dominant giving rise to a signal that has a very weak temperature dependence. We are investigating the possible mechanisms for the observed temperature dependencies.

We estimate that the UV power density of the excitation source at our sample is about 1 mW/cm². Our previous room temperature fiber sensor measurements [4] were made with an incident power density of 9 mW/cm², and the cross sectional area of the fiber sensor was roughly a factor 10 smaller than the illumination spot during our current measurements. From the signal to noise in the measurements shown in **Figure 6**, we anticipate that despite the decrease in the integrated signal intensity with temperature, we will have enough luminescent photons to develop a fiber optic based sensor using Mo-cluster / sol-gel composite films similar to that of sample 15F. We will investigate increasing the cluster concentration and/or making thicker films to increase the signal if that proves to be necessary.

CONCLUSIONS

The potassium salt of Mo₆Cl₁₂ was synthesized and characterized by optical spectroscopy and thermal analysis. The salt has improved thermal stability compared to Mo₆Cl₁₂, and remains luminescent after aging in air at 280 °C. We have demonstrated that immobilization of the Mo₆Cl₁₂ clusters in a sol-gel matrix heated to 200 °C does not effect the quenching of the cluster luminescence by oxygen. The luminescence of Mo₆Cl₁₂ immobilized in a sol-gel matrix was also measured as a function of heater temperature up 200 °C in an inert environment. While the luminescence decreased with temperature, the intensity at 200 °C should be sufficient to enable detection of the luminescence in a optical fiber geometry.

REFERENCES

- [1] R. D. Mussell, Thesis, Michigan State University, 1988
- [2] M. D. Newsham, Thesis, Michigan State University, 1988
- [3] C.R. Ruud, Thesis, Michigan State University, 1999.
- [4] R. N. Ghosh, G. L. Baker, C. J. Ruud, D. G. Nocera, *Appl. Phys. Lett.*, **75**, 2885 (1999)
- [5] Remillard, J.T.; Jones J.R.; Poindexter, B.D.; Narula, C.K.; and Weber, W.H., *Applied Optics*, **38**, no. 25, 5306 (1999)
- [6] J.C. Sheldon *J. Chem. Soc.* 410 (1962)
- [7] J.C. Sheldon *J. Chem. Soc.* 1007 (1961)
- [8] Y. Saito, H. Tanaka, Y. Sasaki and T. Azumi, "Temperature dependence of the luminescence lifetime of hexanuclear Molybdenum (II) Chloride cluster. Identification of lower excited triplet sublevels", *J. Phys. Chem.*, **89**, 4413 - 4415 (1985).

BIBLIOGRAPHY

None.

LIST OF ACRONYMS AND ABBREVIATIONS

$\text{Mo}_6\text{Cl}_{12} \cdot 2\text{CH}_3\text{CN}$ in acetonitrile – Moly Oil

HCl – Hydrochloric Acid

MeOH – Methanol

CH_3CN – Acetonitrile

TEOS – Tetraethyl orthosilicate