

DREXEL UNIVERSITY

# Synthesis and Characterization of Mo<sub>2</sub>GaC, Mo<sub>2</sub>GaN and Mo<sub>2</sub>AlC MAX Phases

**MATE 493**

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## 1.0 Abstract

The goal of this project was to synthesize three new MAX phases: Mo<sub>2</sub>GaC, Mo<sub>2</sub>GaN and Mo<sub>2</sub>AlC. A pure MAX phase of Mo<sub>2</sub>GaC was produced after sintering in an evacuated quartz tube for four weeks at 850°C. Also, peaks were observed in the XRD data corresponding to Mo<sub>3</sub>GaC<sub>2</sub> MAX phase. The ideal thermodynamic conditions for synthesizing both Mo<sub>2</sub>GaN and Mo<sub>2</sub>AlC were not found. Most likely these materials do not exist as MAX phases. However, a pure phase of Mo<sub>3</sub>Al<sub>2</sub>C, a low temperature superconductor was synthesized. A fully dense bulk sample of Mo<sub>2</sub>GaC was not produced. Therefore the material properties of Mo<sub>2</sub>GaC were not characterized. Mo<sub>2</sub>GaC was etched with a 50% concentration of hydrofluoric acid for 96 hours. XRD and EDS both revealed that Gallium was etched from Mo<sub>2</sub>GaC MAX phase. Forming a stable Mo<sub>2</sub>C MXene was shown to be possible.

## 2.0 Introduction

MAX phases are groups of layered ternary carbides and nitrides that follow the formula M<sub>(n+1)</sub>AX<sub>(n)</sub> where *n* is 1, 2 or 3; M is an early transition metal, A is a group A element and X is either carbon or nitrogen [1]. MAX phases are an interesting group of materials that often exhibit properties of both metals and ceramics [1]. For example they are elastically stiff, thermally and electrically conductive with relatively low thermal expansion coefficients. Also, they are relatively soft, thermal shock resistant and damage tolerant [2].

Nowotny produced over 50 of these MAX phases in the 1960's [3]. He did not characterize their material properties, however. Almost three decades later, Barsoum rediscovered this group of materials and learned how to produce them in bulk. This important step led to the understanding of their unique material properties [1]. Since 1995, Barsoum et al synthesized in bulk and characterized about 20 MAX phases [4].

MXene's are two-dimensional flakes of MAX phases that have been etched with hydrofluoric acid to remove layers of A group elements, resulting in very high specific surface areas [5]. Mo<sub>2</sub>GaC, Mo<sub>2</sub>GaN and Mo<sub>2</sub>AlC once synthesized, could be great candidates for producing molybdenum carbides MXenes. Molybdenum carbides are utilized in the dry reforming of methane to produce hydrogen gas [6]. They are also used as a catalyst for the water gas shift, the reaction of CO with H<sub>2</sub>O to form CO<sub>2</sub> and H<sub>2</sub> [7]. Due to the increase in H<sub>2</sub> demand, both these processes are important. Molybdenum carbides also show great electrochemical potential [8]. Mo<sub>2</sub>C MXene will have a larger specific surface area than Mo<sub>2</sub>C, which is desirable when used as an electrode material for energy storage or as a catalyst for chemical reactions.

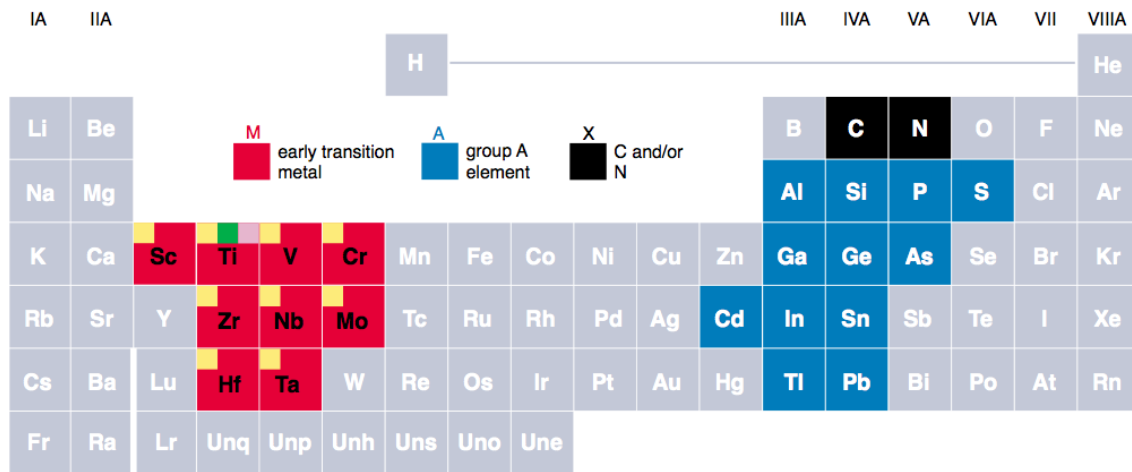
This project aimed to synthesize and characterize Mo<sub>2</sub>GaC, Mo<sub>2</sub>AlC and Mo<sub>2</sub>GaN. The latter two would be the first MAX phases of these materials. The former was produced by Toth in the 1960's and was shown to have low temperature superconductive properties [9]. These molybdenum carbide and

nitride MAX phases would produce molybdenum carbide MXenes, which have potential for electrochemical applications and as catalysts in the formation of H<sub>2</sub>.

### 3.0 Background

#### 3.1 MAX Phase

MAX phases are layered, machinable ternary carbide, nitride or carbonitride materials. The name MAX derives from the material composition, being made up of an early transition metal, M, a group A, typically IIIA or IVA, and either Carbon and/or Nitrogen, X [1]. Figure 1 clearly shows M, A and X elements.



**Figure 1:** This periodic table of elements shows the three components of MAX phases. Highlighted in red are M elements, early transition metals. A elements are blue, group A elements. X elements are black, either C or N or C and N [1].

MAX phases follow the formula  $M_{(n+1)}AX_n$  where  $n$  is 1, 2 or 3. Based on this formula MAX phases are subdivided into three groups, 211, 312 or 413 depending on the value of  $n$ . These subgroups are shown in Figure 2.

211	Ti <sub>2</sub> AlC*		Ti <sub>2</sub> AlN*		Hf <sub>2</sub> PbC*		Cr <sub>2</sub> GaC		V <sub>2</sub> AsC		Ti <sub>2</sub> InN	
	Nb <sub>2</sub> AlC*		(Nb,Ti) <sub>2</sub> AlC*		Ti <sub>2</sub> AlN <sub>0.5</sub> C <sub>0.5</sub> *		Nb <sub>2</sub> GaC		Nb <sub>2</sub> AsC		Zr <sub>2</sub> InN	
	Ti <sub>2</sub> GeC*		Cr <sub>2</sub> AlC		Zr <sub>2</sub> SC		Mo <sub>2</sub> GaC		Ti <sub>2</sub> CdC		Hf <sub>2</sub> InN	
	Zr <sub>2</sub> SnC*		Ta <sub>2</sub> AlC		Ti <sub>2</sub> SC		Ta <sub>2</sub> GaC*		Sc <sub>2</sub> InC		Hf <sub>2</sub> SnN	
	Hf <sub>2</sub> SnC*		V <sub>2</sub> AlC		Nb <sub>2</sub> SC		Ti <sub>2</sub> GaN		Ti <sub>2</sub> InC		Ti <sub>2</sub> TiC	
	Ti <sub>2</sub> SnC*		V <sub>2</sub> PC		Hf <sub>2</sub> SC		Cr <sub>2</sub> GaN		Zr <sub>2</sub> InC		Zr <sub>2</sub> TiC	
	Nb <sub>2</sub> SnC*		Nb <sub>2</sub> PC		Ti <sub>2</sub> GaC		V <sub>2</sub> GaN		Nb <sub>2</sub> InC		Hf <sub>2</sub> TiC	
	Zr <sub>2</sub> PbC*		Ti <sub>2</sub> PbC*		V <sub>2</sub> GaC		V <sub>2</sub> GeC		Hf <sub>2</sub> InC		Zr <sub>2</sub> TiN	

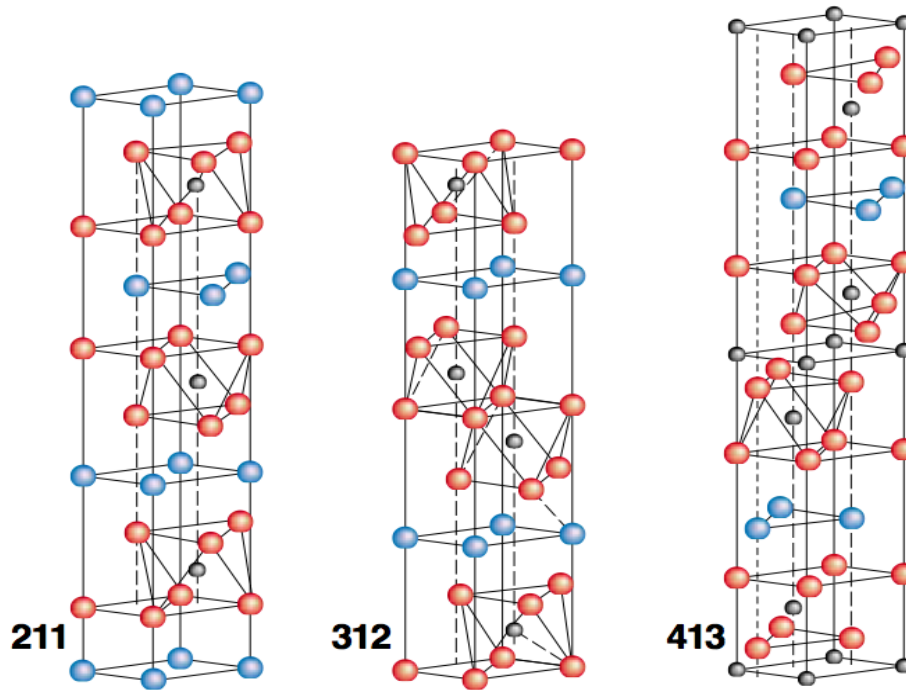
312	Ti <sub>3</sub> AlC <sub>2</sub> *		Ti <sub>3</sub> GeC <sub>2</sub> *	
	Ti <sub>3</sub> SiC <sub>2</sub> *			

413	Ti <sub>4</sub> AlN <sub>3</sub> *	

**Figure 2:** The three subgroups of MAX phases: 211, 312

The three subgroups of these materials have slightly different crystal structures. All three have a certain number of metal carbide or nitride layers separated by an A-group layer. The A-group layers in each subgroup are separated by  $(n + 1)$  of either metal carbide or nitride layers corresponding to the MAX formula. In other words, every third layer is an A-group for 211, every fourth layer is an A-group for 312 and every fifth layer is an A-group for 413 [1]. This is illustrated in Figure 3.



**Figure 3: Metal carbide and nitride layers are depicted as red and black layers. A-group layers are blue. Every third layer in 211 is A-group, every fourth in 312 and every fifth in 413 [1].**

MAX phases exhibit very interesting physical, mechanical and electrical properties. For example, at room temperature MAX phases can be loaded with stresses up to 1GPa and when unloaded they fully recover [2]. For a ceramic, this is quite remarkable.

## 4.0 Initial Method

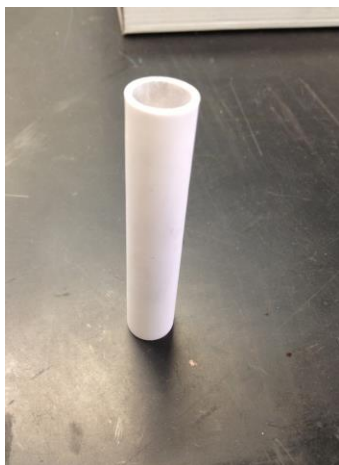
### 4.1 Initial Experimental Plans and Procedures

Three potential MAX phases were attempted to be synthesized: Mo<sub>2</sub>GaC, Mo<sub>2</sub>GaN and Mo<sub>2</sub>AlC. MAX phases, if sintered at too high of a temperature dissociate. If the temperature is too low, very long times are required to reach a full reaction. A balance between temperature and time must be reached. With these materials there were three variables that were controlled: composition, temperature and time. The composition was fixed for each experiment leaving temperature and time. Limiting the variables to two increased chances of determining the ideal thermodynamic conditions to produce these materials.

Characterization went hand in hand with varying the experimental conditions. A few samples were produced and characterized using X-ray Diffraction (XRD) to determine composition. The experimental parameters were then altered as conclusions were reached concerning the composition of the materials produced.

According to the literature Mo<sub>2</sub>GaC MAX phase can be produced with the following experimental procedures [9]. A 2:1:1 molar elemental mixture of powdered molybdenum, liquid gallium and powdered carbon was combined in an evacuated quartz tube and sintered at 850°C for four weeks [9]. One sample of 10.00g was sealed in evacuated quartz tubing and sintered at 850°C for one week. This sample was analyzed with XRD to determine if the evacuated quartz tubing was sealed properly.

The main problem that was faced with sealing these samples in evacuated quartz tubing is the limitations of the glass blower. The glass blowing shop was not equipped to pull vacuum on fine powders. The powders were removed from the quartz tubing, adversely affecting the stoichiometry. To circumvent this the sample was placed in a cylindrical alumina crucible as shown in figure 8. The quartz tube was prepped by the glass blower, one end necked down to pull vacuum while both ends will be left open as shown in figure 9.



**Figure 8: The elemental powder mixture was loaded into this alumina crucible, which was inserted into a quartz tube.**



**Figure 9: A quartz tube was necked down on one end while both ends were left open. The alumina crucible was inserted into the larger end and vacuum was pulled on the smaller**

The sample was loaded into the alumina crucible, which was inserted into the top of the quartz tubing. The top of the tube was sealed while upright. Then vacuum was pulled from the bottom and the tube was sealed at the top of the neck.

Since the aforementioned experiment was time intensive concurrent experiments were run in the hope that far shorter times will be required to produce Mo<sub>2</sub>GaC MAX phase. In these experiments time was fixed at two hours while temperature was set at 1000°C, 1300°C and 1600°C. An elemental powder mixture of gallium and carbon was placed in an alumina crucible. Solid gallium was placed

on top of the powder mixture and inserted into a tube furnace. The tube furnace maintained an inert argon environment at atmospheric pressure. As the temperature of the furnace increased liquid gallium floated on top of the powder mixture and reacted with the other two elements. The resulting materials were characterized with XRD and the appropriate temperature and time were adjusted according to the compositions of the materials.

Meanwhile, 9.15g of a 2:1:1 molar mixture of powdered molybdenum and gallium nitride were combined along with 15 steel milling balls 10mm in diameter and placed into a polyethylene jar. This jar was placed onto a milling machine for 24 hours to ensure a homogeneous mixture of molybdenum and gallium nitride. After, this mixture was loaded into an alumina crucible and inserted into a horizontal tube furnace. This furnace was sealed and filled with a constant flow of argon at atmospheric pressure. The outflow of argon bubbled through a blowback valve, an Erlenmeyer flask filled with water. The time was fixed at two hours and the temperature was set at 1000°C, 1300°C and 1600°C respectively. Again, the resulting materials were studied with XRD and based on the composition of the materials thermodynamic conditions of the experiment were adjusted.

Finally, 59.30g of a 2:1.1:1 molar elemental ratio of molybdenum, aluminum and carbon powder mixture was prepared. According to the literature a 10% molar excess of the A-group element should result in a better chance producing a MAX phase [12]. This mixture was then placed in a polyethylene jar and 15 steel milling balls 10mm in diameter were added. Next, this loaded jar was placed on a mill for 24 hours to fully mix the powder. Then, three samples of 19.00g each were placed into a small alumina crucible. This crucible was loaded into a tube furnace with an argon flow as described previously. The temperature was set at 1000°C, 1300°C and 1600°C respectively while the time was fixed at two hours. These samples were studied with XRD and depending upon the results the thermodynamic conditions were varied accordingly.

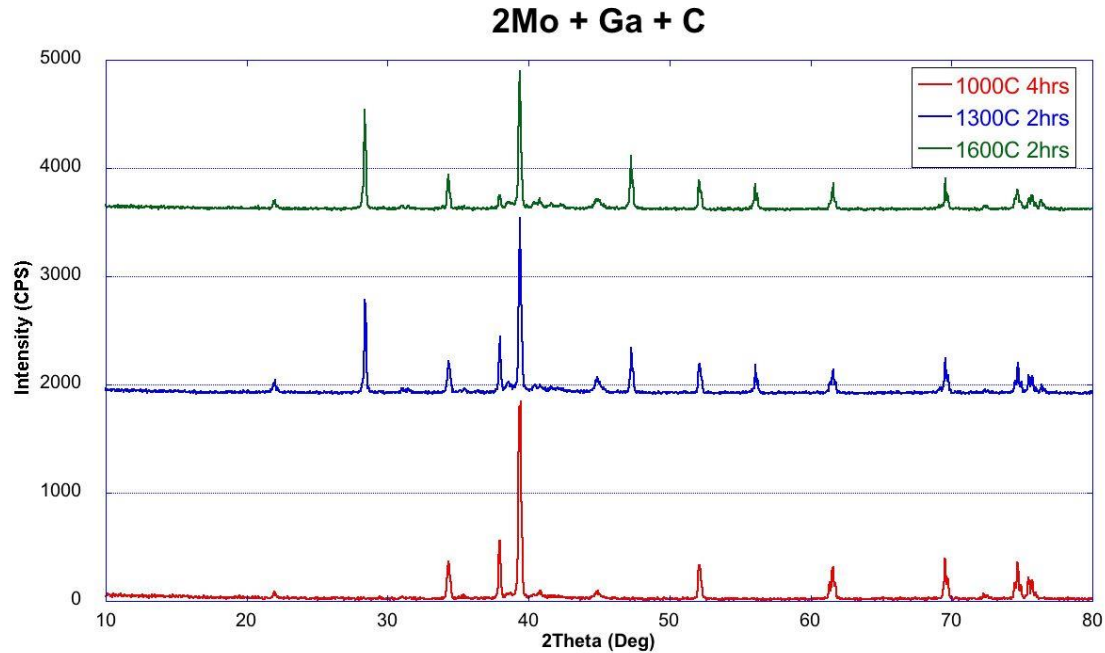
## **4.2 Characterization**

Post-synthesis, powder samples were prepared with 10 wt.% silicon powder to serve as a reference to the composition of the materials being characterized. Scans were run from 5° to 80° with a step size of 0.04 for 1.0 second. This produced an adequate XRD pattern to identify the phases of the material.

## 5.0 Initial Results

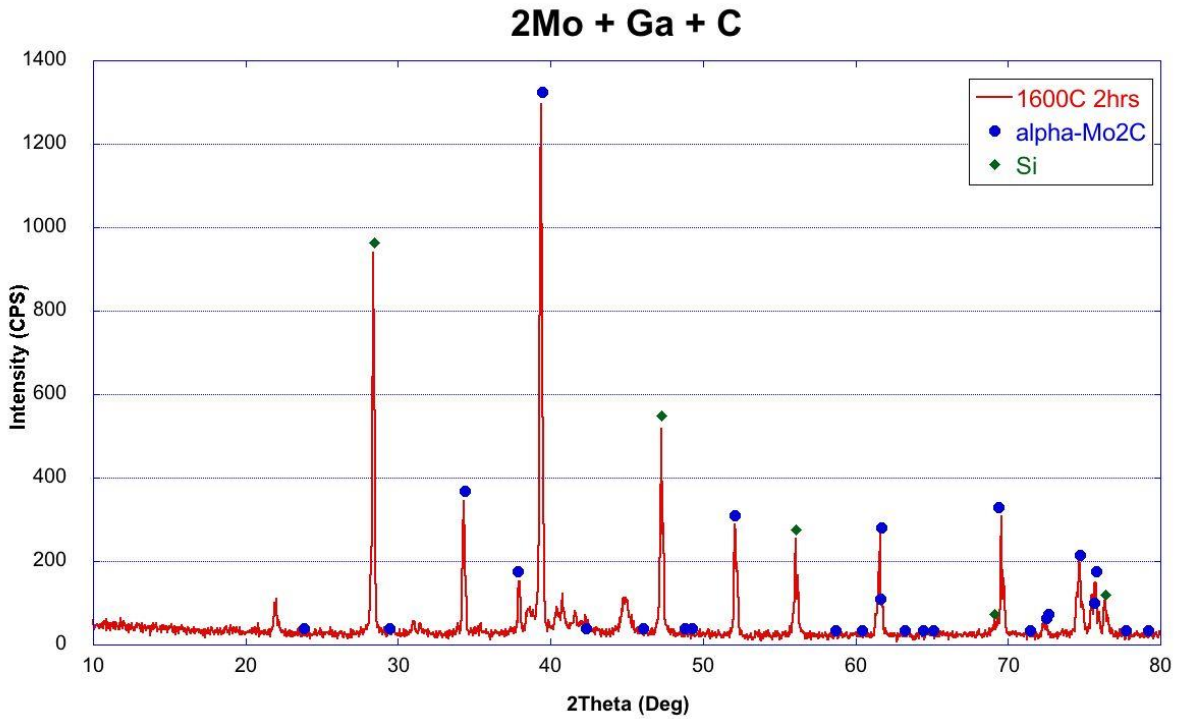
### 5.1 2Mo+Ga+C

The following XRD data is from three samples synthesized in the tube furnace at 1600°C for four hours, 1300°C for two hours and 1000°C for two hours. Also, the last XRD graph in this section is the sample sealed in evacuated quartz tubing and sintered at 850°C for one week.



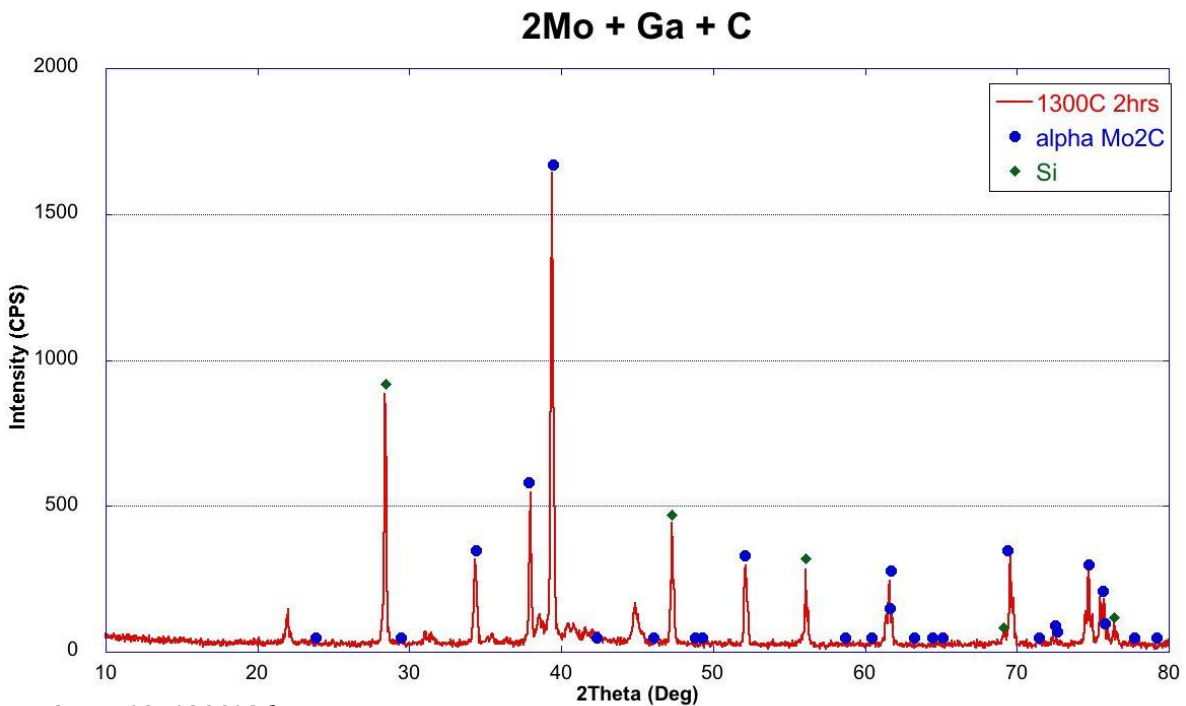
**Figure 10: XRD Patterns**

The three XRD patterns are graphed together showing the change based on temperature. (Note, 1000°C for four hours was analyzed without 10wt% Si. This was not intentional, but done in error.) As a result the peaks at  $2\theta \sim 28^\circ$ ,  $\sim 46^\circ$  and  $\sim 55^\circ$  are not observed. The rest of the peaks are found in all three samples.



**Figure 11: 1600°C for Two Hours**

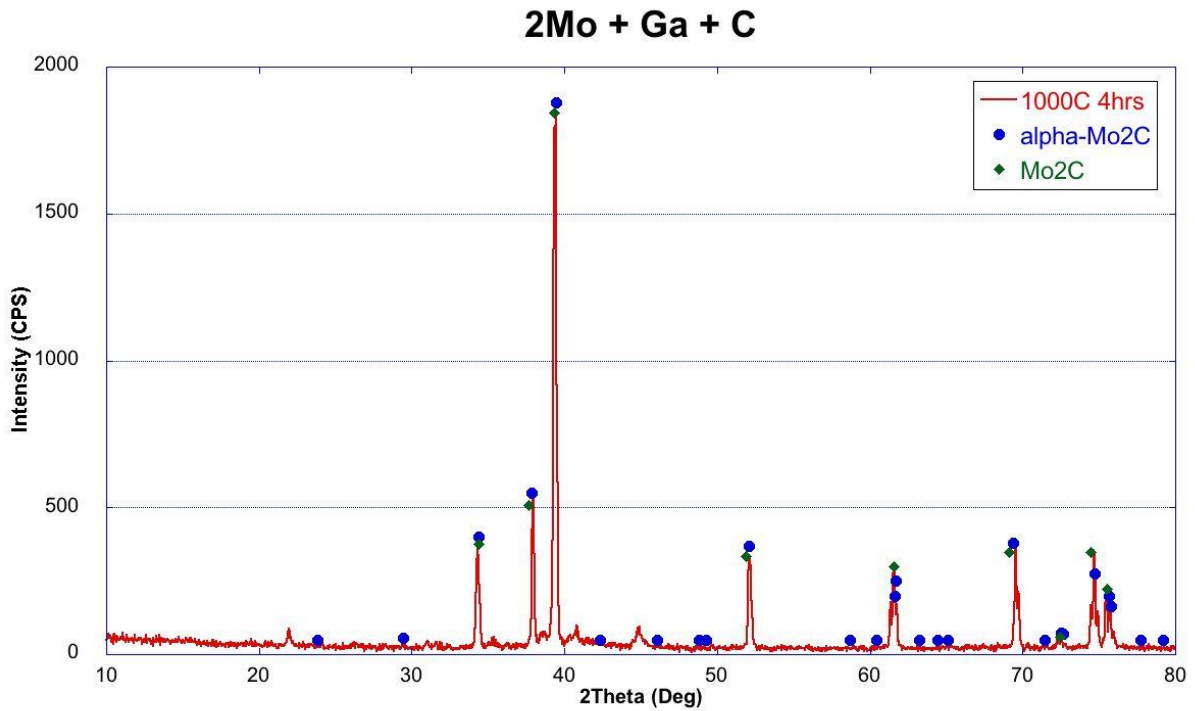
The XRD pattern is shown with the corresponding phases identified. At 1600°C for two hours the resulting phase is the alpha phase of Mo<sub>2</sub>C.



**Figure 12: 1300°C for Two Hours**

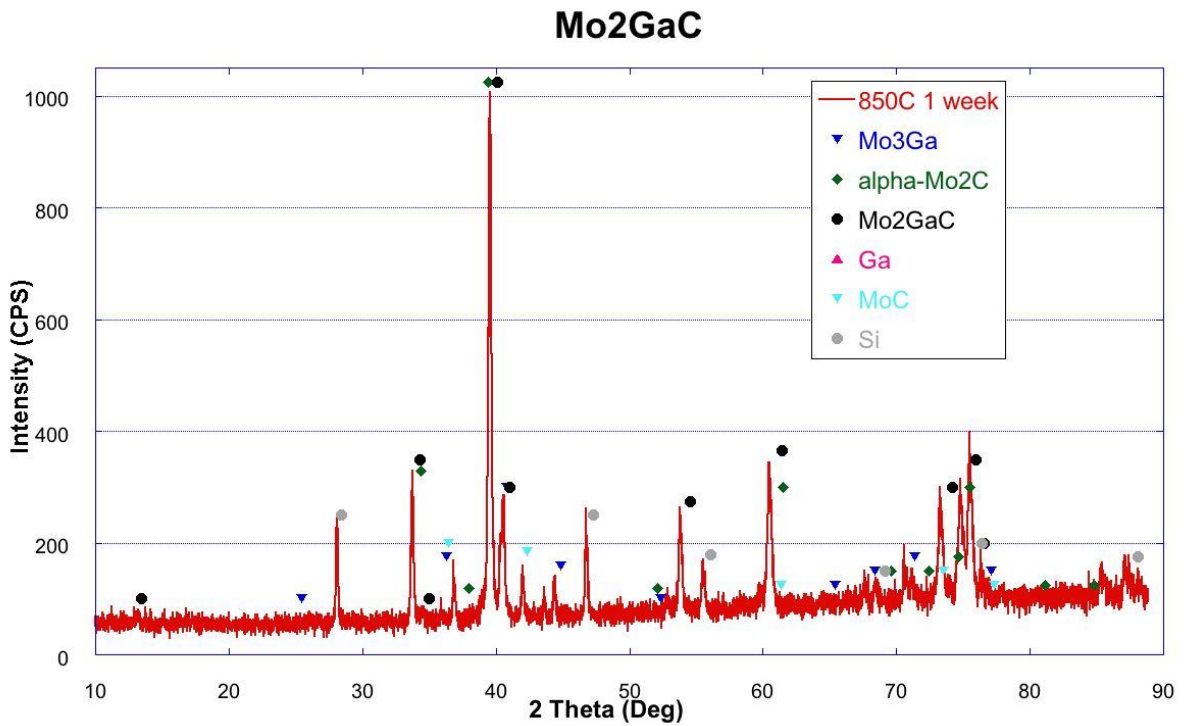
The XRD pattern is shown with the corresponding phases identified. Just as in the sample prepared at 1600°C the resulting phase is alpha Mo<sub>2</sub>C. A lower temperature did not produce the desired 211 MAX phase.





**Figure 13: 1000°C for Four Hours**

After four hours at 1000°C in the tube furnace the resulting material was found to be Mo<sub>2</sub>C. A decrease in temperature did not produce favorable thermodynamic conditions for the formation of Mo<sub>2</sub>GaC MAX phase.

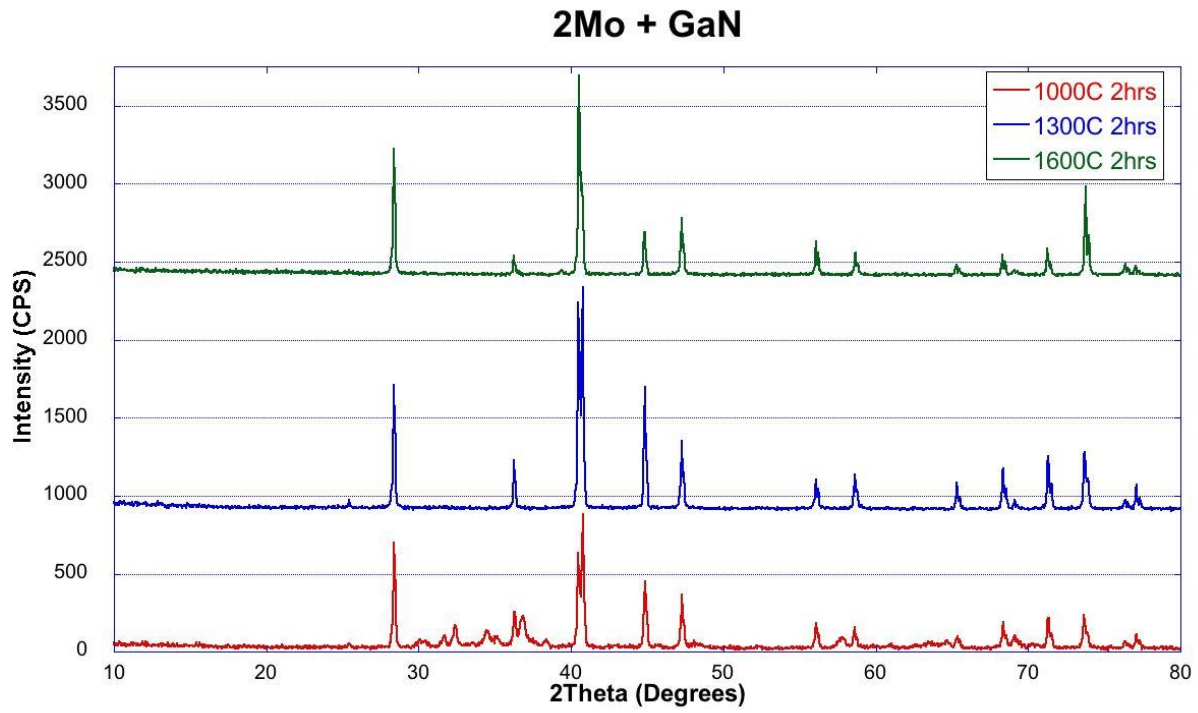


**Figure 14: 850°C for One Week**

This sample was sealed in an evacuated quartz tube and sintered at 850°C for one week. Peaks corresponding to Mo<sub>2</sub>GaC MAX phases were observed as well as four other phases. These results were the first favorable results found.

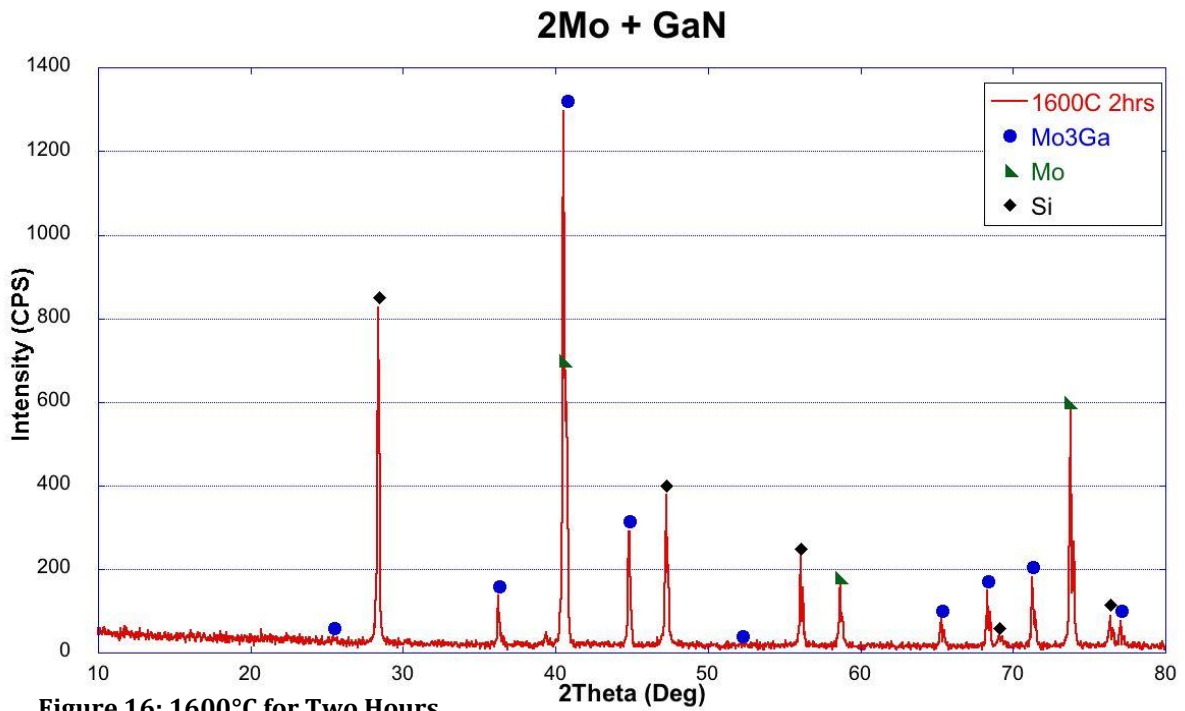
## 5.2 2Mo+GaN

The following XRD data corresponds to three samples sintered in the tube furnace for two hours at 1600°C, 1300°C and 1000°C.



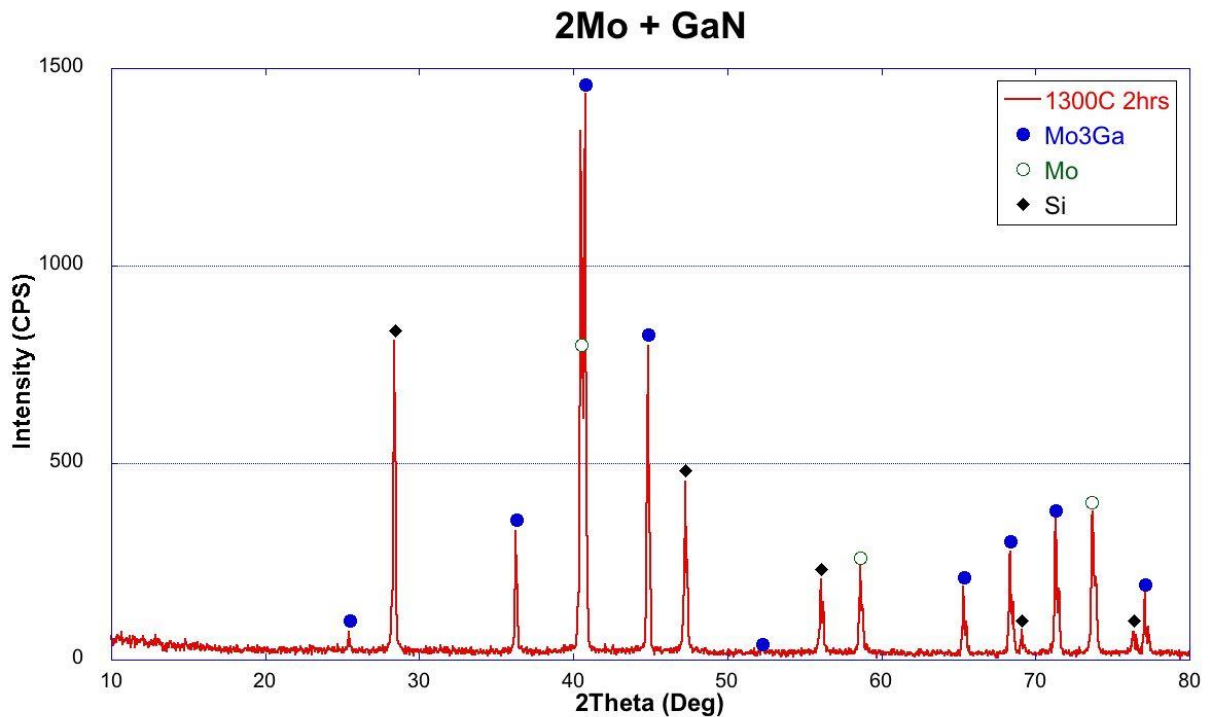
**Figure 15: XRD Patterns**

The three corresponding XRD patterns for 1600°C, 1300°C and 1000°C are compared in this figure. The sample sintered at 1000°C for two hours resulted in a much noisier XRD pattern.



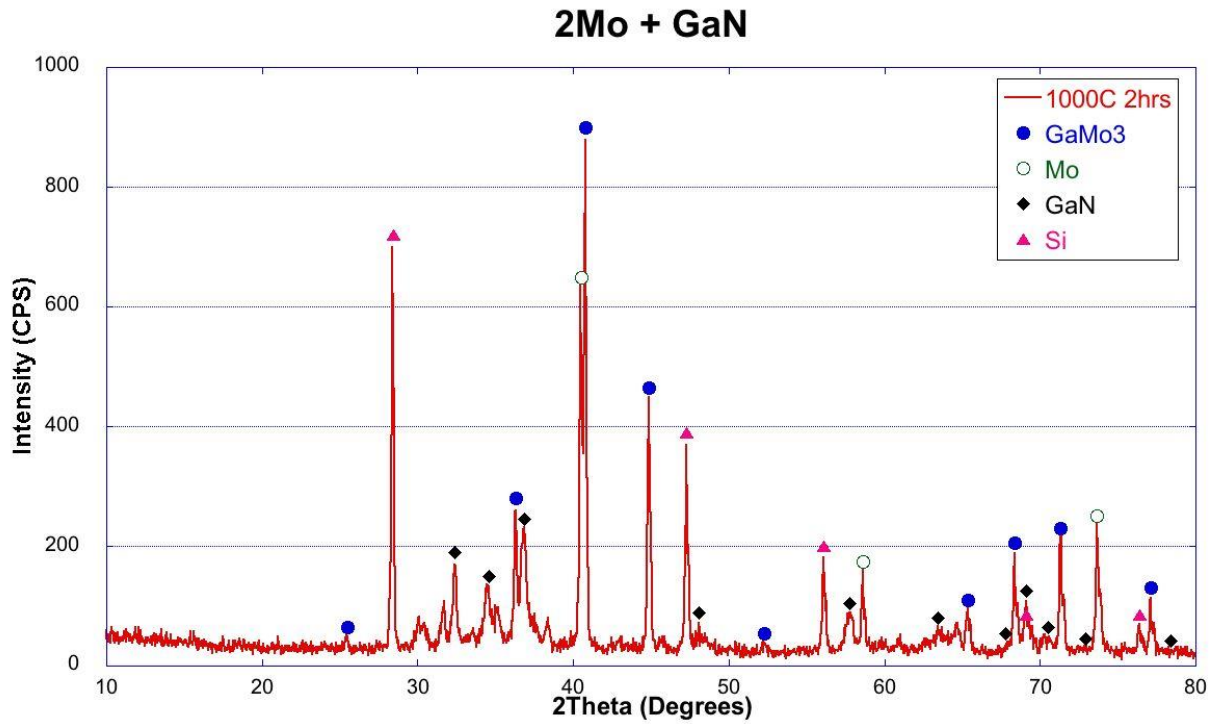
**Figure 16: 1600°C for Two Hours**

The XRD pattern is shown along with the peaks identified by the corresponding phases. After two hours at 1600°C in the tube furnace the primary phase identified is  $\text{Mo}_3\text{Ga}$ . There is also some unreacted Mo.



**Figure 17: 1300°C for Two Hours**

The XRD pattern is shown along with the identified peaks corresponding to the correct phases. After two hours at 1300°C in the tube furnace the primary phase identified is  $\text{Mo}_3\text{Ga}$ . This is identical to the sample sintered at 1600°C for two hours.

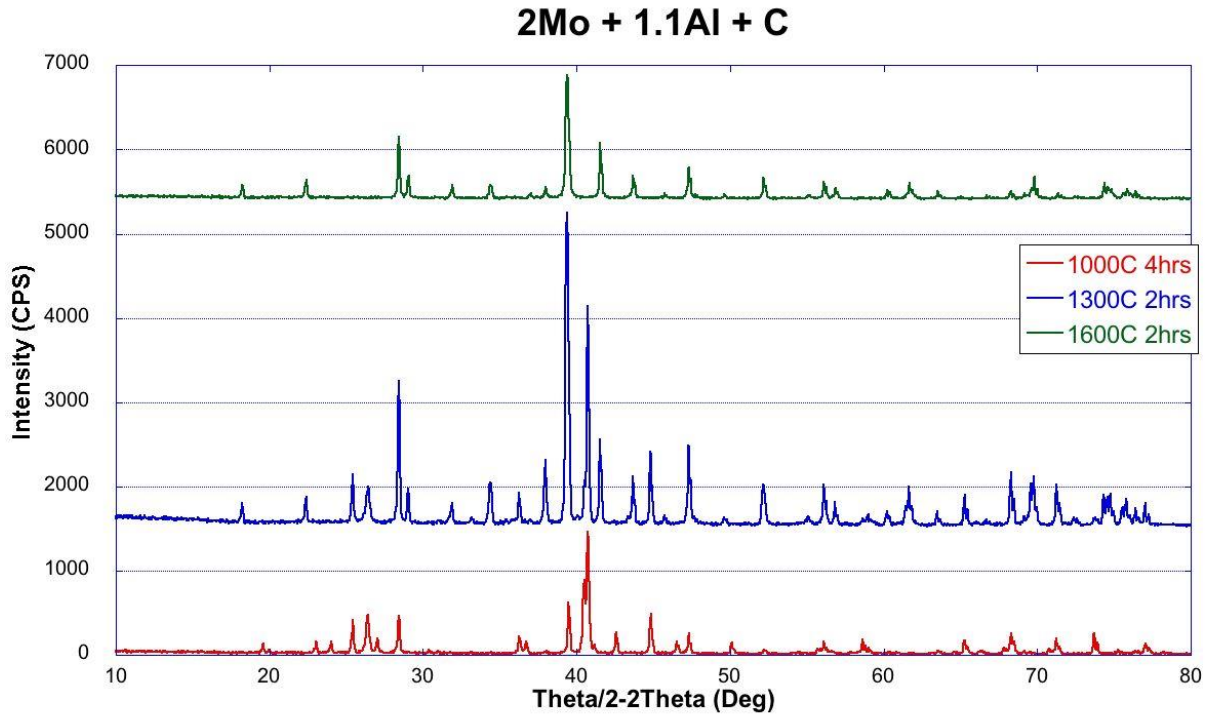


**Figure 18: 1000°C for Two Hours**

The XRD pattern shown here along with the three phases identified shows that at 1000°C for two hours Mo<sub>3</sub>Ga is the dominant phase. There is also unreacted GaN and Mo.

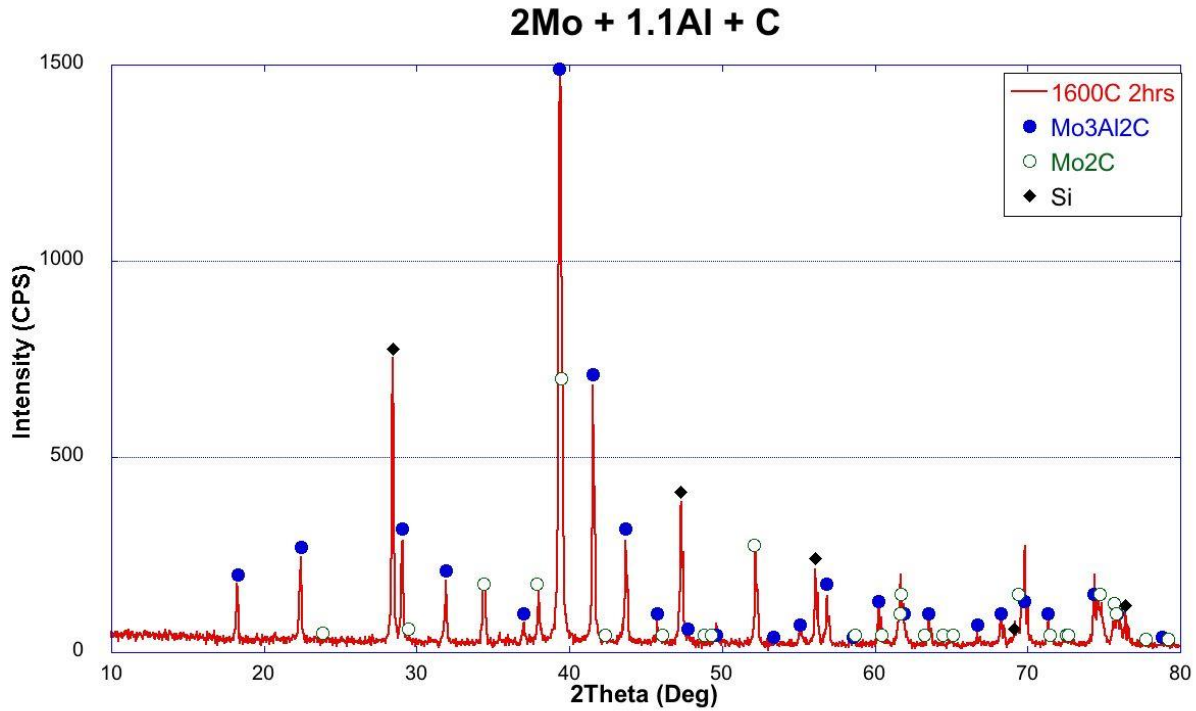
### 5.3 2Mo+1.1Al+C

The following XRD patterns correspond to three samples sintered in the tube furnace at 1600°C for two hours, 1300°C for two hours and 1000°C for four hours. Note that excess Al was used in each sample to promote the synthesis of a MAX phase.



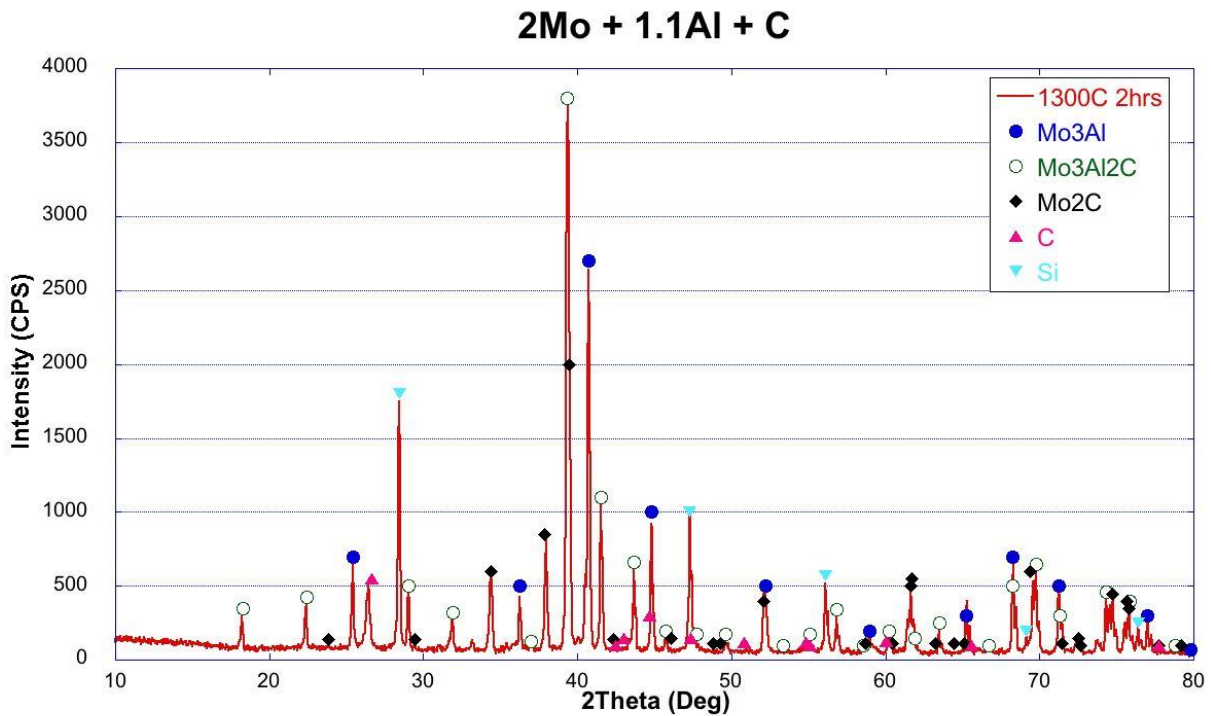
**Figure 19: XRD Patterns**

The three XRD patterns are shown for 1000°C, 1300°C and 1600°C. The changes based on temperature can be seen.



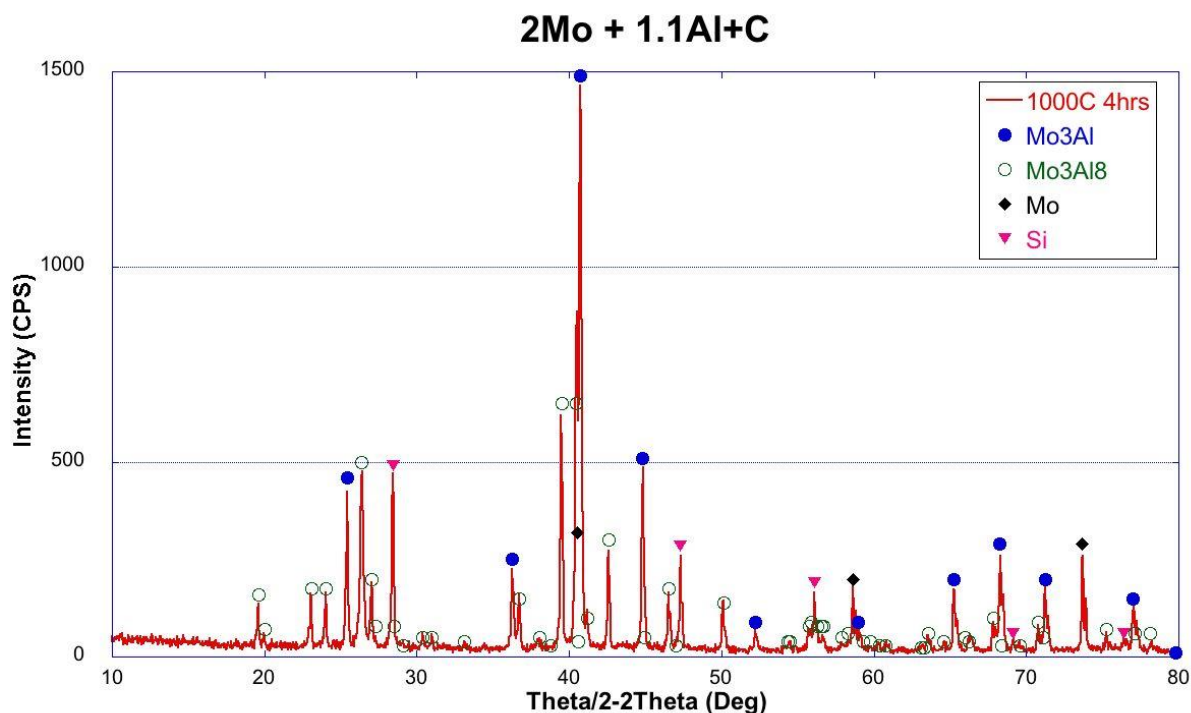
**Figure 20: 1600°C for Two Hours**

The XRD pattern is shown. The primary phase identified is  $\text{Mo}_3\text{Al}_2\text{C}$  along with  $\text{Mo}_2\text{C}$ . This temperature did not produce a MAX phase.



**Figure 21: 1300°C for Two Hours**

The XRD pattern shows several phases of materials present in this sample. Like 1600°C there is  $\text{Mo}_3\text{Al}_2\text{C}$ . However it is no longer the dominant phase.



**Figure 22: 1000°C for Two Hours**

Unlike the previous two figures, this XRD pattern does not show  $\text{Mo}_3\text{Al}_2\text{C}$ . This temperature is too low to cause a full reaction with Mo, Al and C. Primarily  $\text{Mo}_3\text{Al}$  is present. C did not react at all.

## 6.0 Discussion of Initial Results

### 6.1 2Mo+Ga+C

Based on the results of XRD at all three temperatures only  $\text{Mo}_2\text{C}$  was produced. For both 1300°C and 1600°C the alpha phase of  $\text{Mo}_2\text{C}$  was found. It was surprising that gallium was not present in any of these materials. This leads to the conclusion that either gallium required a sealed environment or lower temperatures to react favorably with molybdenum and carbon.

All of these runs were extremely messy, especially the two higher temperatures. The inside of the tube in the furnace was coated with a large amount of dark powder. Gallium, while below its boiling temperature of 2403°C, seemed to bubble significantly at these temperatures. This physical reaction expelled both gallium and carbon powder from the alumina crucible, coating the inside of the tube furnace.

The sample sealed in evacuated quartz tubing and sintered for one week at 850°C revealed promising results. This was surprising given how poorly the sample was sealed in the evacuated quartz tubing. The glass blower had to turn the tube over, spilling powder outside of the crucible. This can be seen in figure 23. The molar ratio inside and outside the crucible could not be determined. Although there were several phases present,  $\text{Mo}_2\text{GaC}$  MAX phase was identified. A new method of

containing the sample within the alumina crucible and sealing in an evacuated quartz tube was required for all further experiments.



**Figure 23: Crucible Sealed in Evacuated Tube**  
This figure showed the amount of powder outside of the crucible. A much more effective method of containing the elemental mixture was required.

## 6.2 2Mo+GaN

The only new phase identified in the three different temperatures was  $\text{Mo}_3\text{Ga}$ . Based on XRD there was no evidence of nitrides in these samples. It was interesting that GaN dissociated; allowing the gallium to react with molybdenum while the nitrogen disappeared. Based on the intensity of the peaks it appeared that  $\text{Mo}_3\text{Ga}$  has the highest concentration at  $1300^\circ\text{C}$ .

All three temperatures resulted in a semi-solid powder form. The solidity of this formed powder increased with temperature. All three were easily broken apart by hand and ground back into powder.

While  $\text{Mo}_3\text{Ga}$  was not desired initially it was utilized to attempt to synthesize  $\text{Mo}_3\text{GaC}_2$ . Further experiments were conducted sintering  $\text{Mo}_3\text{Ga}$  with the appropriate molar ratio of C. Most likely  $\text{Mo}_2\text{GaN}$  does not exist. All focus was placed on using  $\text{Mo}_3\text{Ga}$  to produce 312 MAX phase, a novel MAX phase.

## 6.3 2Mo + 1.1Al + C

In both the  $1300^\circ\text{C}$  and the  $1000^\circ$  all three elements bonded together to form  $\text{Mo}_3\text{Al}_2\text{C}$ . At  $1300^\circ\text{C}$  the final material was somewhat solid, but easily broken apart by hand. However, XRD showed a small amount of aluminum molybdenum carbide in the materials, but not as much as  $\text{Mo}_3\text{Al}$ .

At  $1600^\circ\text{C}$   $\text{AlMo}_3$  was no longer a phase within the material. It was present in both  $1000^\circ\text{C}$  and  $1300^\circ\text{C}$ . Both of these lower temperatures had a percentage of unreacted elements, either molybdenum or carbon. However, at  $1600^\circ\text{C}$  there were no individual elements. This was promising. This material was also very dense. It took considerable drilling to get powder to perform XRD. The next step taken was altering the stoichiometry to 3:2:1 Mo, Al and C to produce a pure phase of  $\text{Mo}_3\text{Al}_2\text{C}$ , which had never been done before.

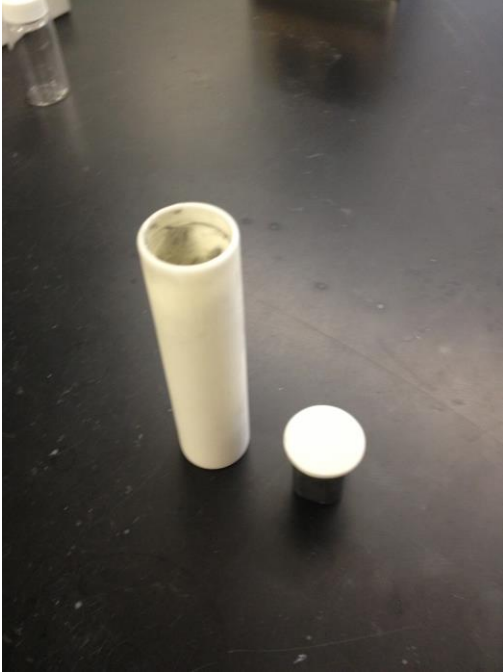
Although the aluminum molybdenum carbide produced was not a MAX phase it is still of interest. This phase has superconductivity behavior at low temperatures [15].



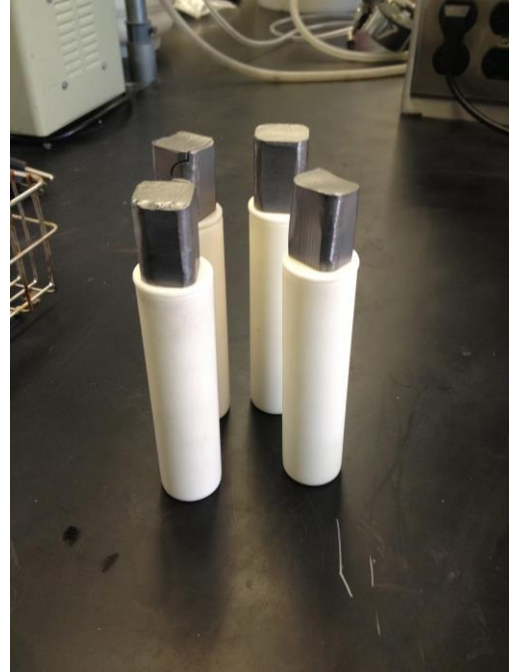
## 7.0 Secondary Method

### 7.1 Secondary Experimental Plans and Procedures

A new method of containing 2Mo+Ga+C within the alumina cylinder and sealing within an evacuated quartz tube was necessary. An alumina disc, as seen in figure 24, was attached to the top of the alumina cylinder with cyanoacrylate. In case the cyanoacrylate burned off while one end of the quartz tube was sealed a weight of 312 MAX phase was placed on top of the alumina disc. This is illustrated in figure 25.



**Figure 24: Alumina Cylinder and Disc**  
This 25mm alumina disc was used as a lid to seal the alumina cylinder. It was attached with cyanoacrylate.



**Figure 25: Sealed Cylinders with Weight**  
Four sealed cylinders are shown. The 312 MAX phase weights held the alumina disc in place if the super glue failed.

Four samples were placed in a bench-top furnace at 850°C for four weeks. Each sample was 40.00g of 2Mo+Ga+C in a 2:1:1 molar ratio. Powdered Mo and C were ball milled for 24 hours and solid Ga was added to each sample. These were degassed in a vacuum furnace for 12 hours. One sample was removed from the bench-top furnace each week and XRD characterized the resulting materials. This provided a thorough understanding of the thermodynamic reactions that took place over the course of the experiment.

The stoichiometry of 2Mo+1.1Al+C was adjusted to 3Mo+2Al+C to produce a pure phase of  $\text{Mo}_3\text{Al}_2\text{C}$ . Powdered Mo, Al and C were ball milled for 24 hours in a 3:2:1 molar ratio. Two samples of 50.00g were placed in alumina crucibles and inserted into a tube furnace in an inert argon atmosphere. One sample was sintered

for two hours at 1600°C and the other was sintered for two hours at 1450°C. XRD characterized the resulting materials.

## 8.0 Secondary Results

### 8.1 2Mo+Ga+C at 850°C

The following XRD patterns are of four samples sealed in evacuated quartz tubing with the secondary design method and sintered at 850°C for one, two, three and four weeks.

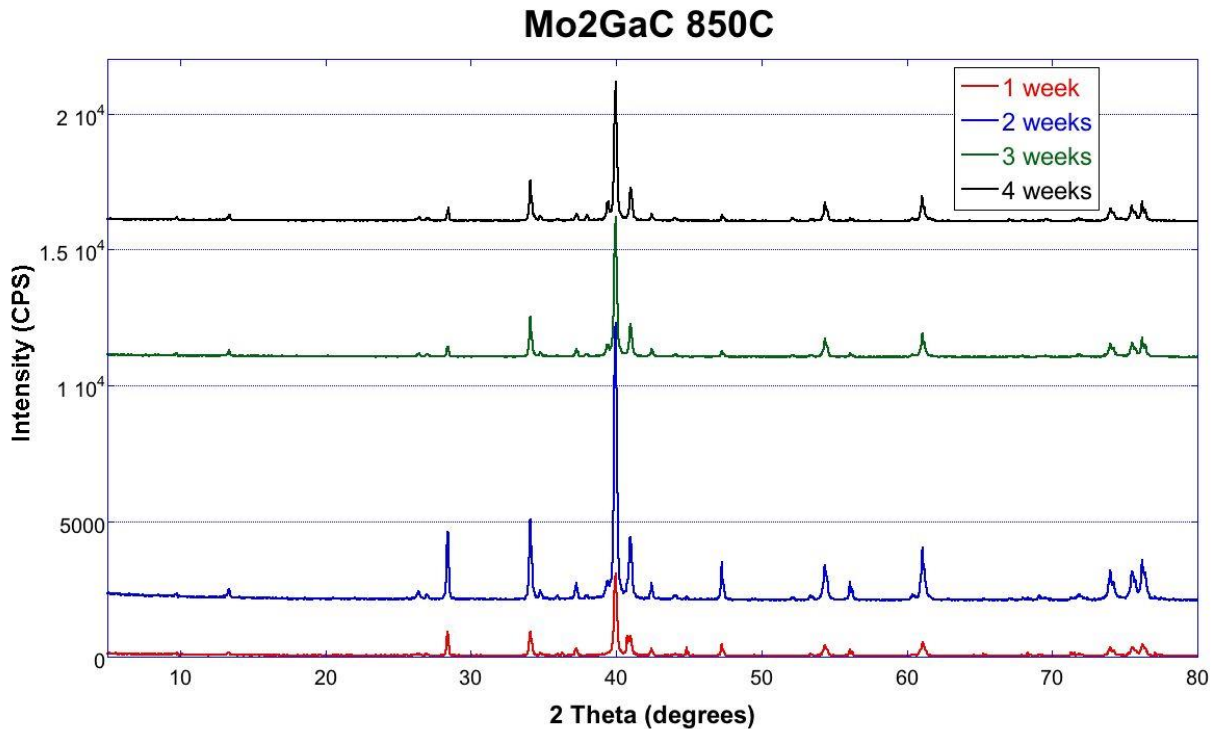
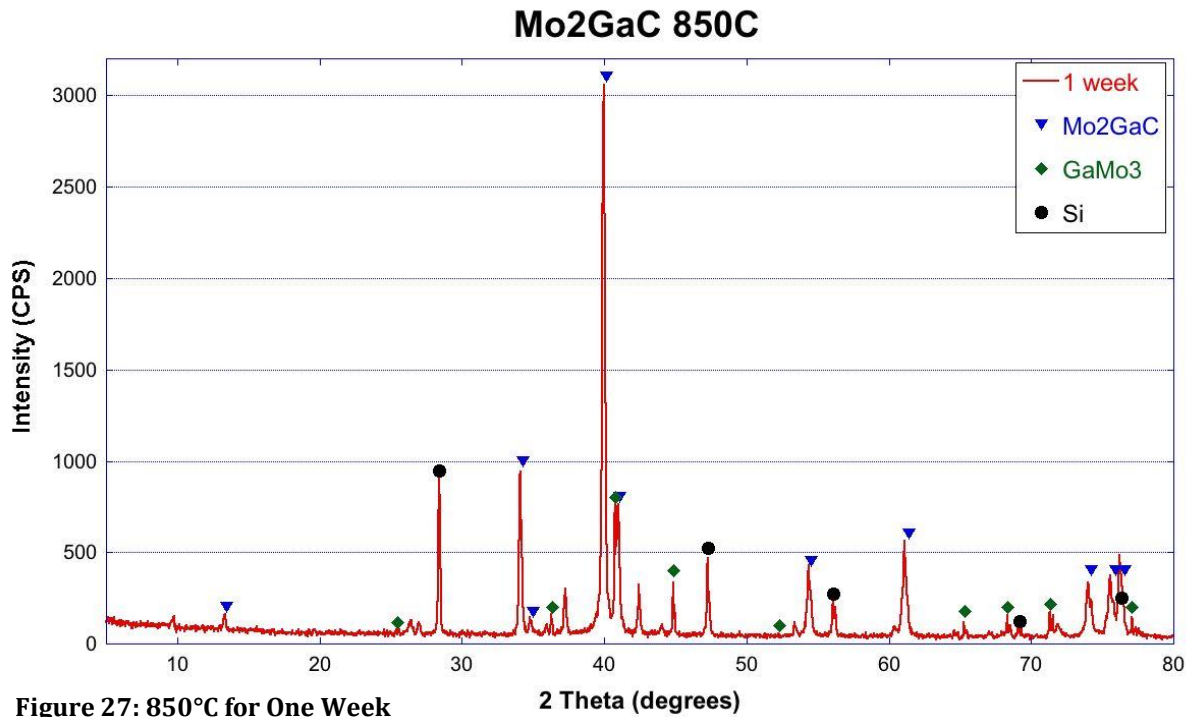
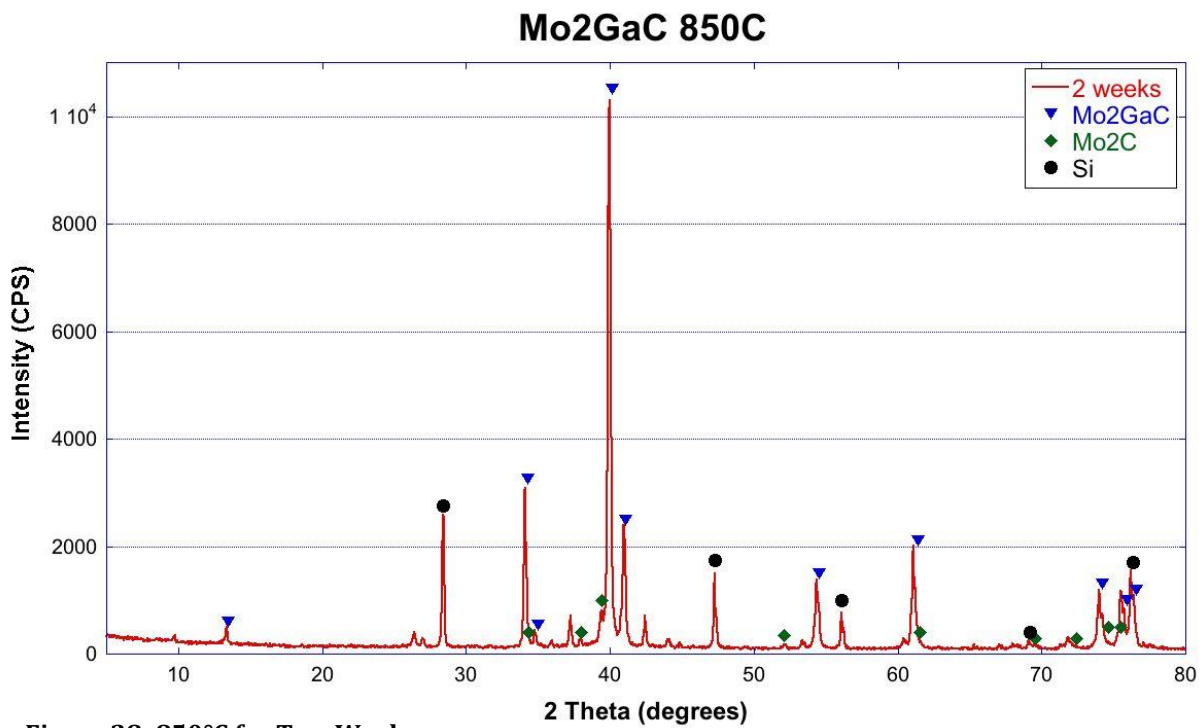


Figure 26: 850°C for One, Two, Three and Four Weeks

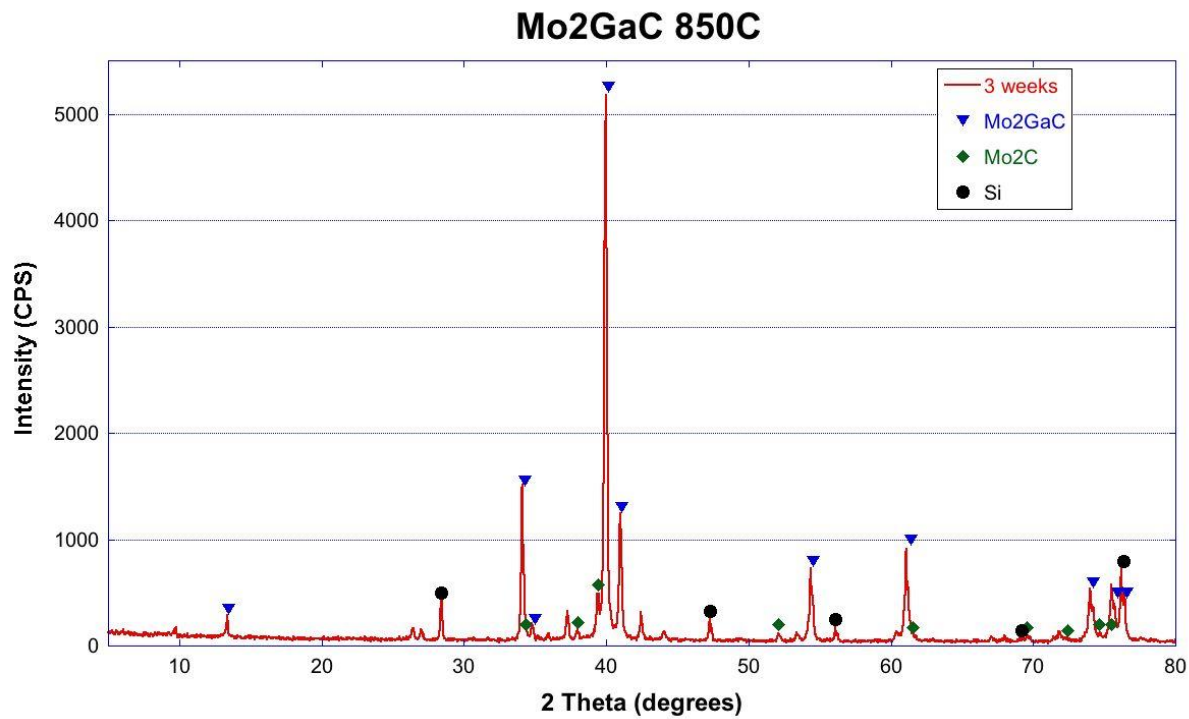
There was great correlation between these four XRD patterns. With each week the XRD pattern was cleaner, ultimately resulting in a pure phase of Mo<sub>2</sub>GaC after four weeks. Also, in each case, there was a peak at 2θ~9° which corresponded to a 312 MAX phase of Mo<sub>3</sub>GaC<sub>2</sub>.



**Figure 27: 850°C for One Week**  
 After one week with the new method Mo<sub>2</sub>GaC MAX phase was produced as well as Mo<sub>3</sub>Ga with the MAX phase being the primary phase.

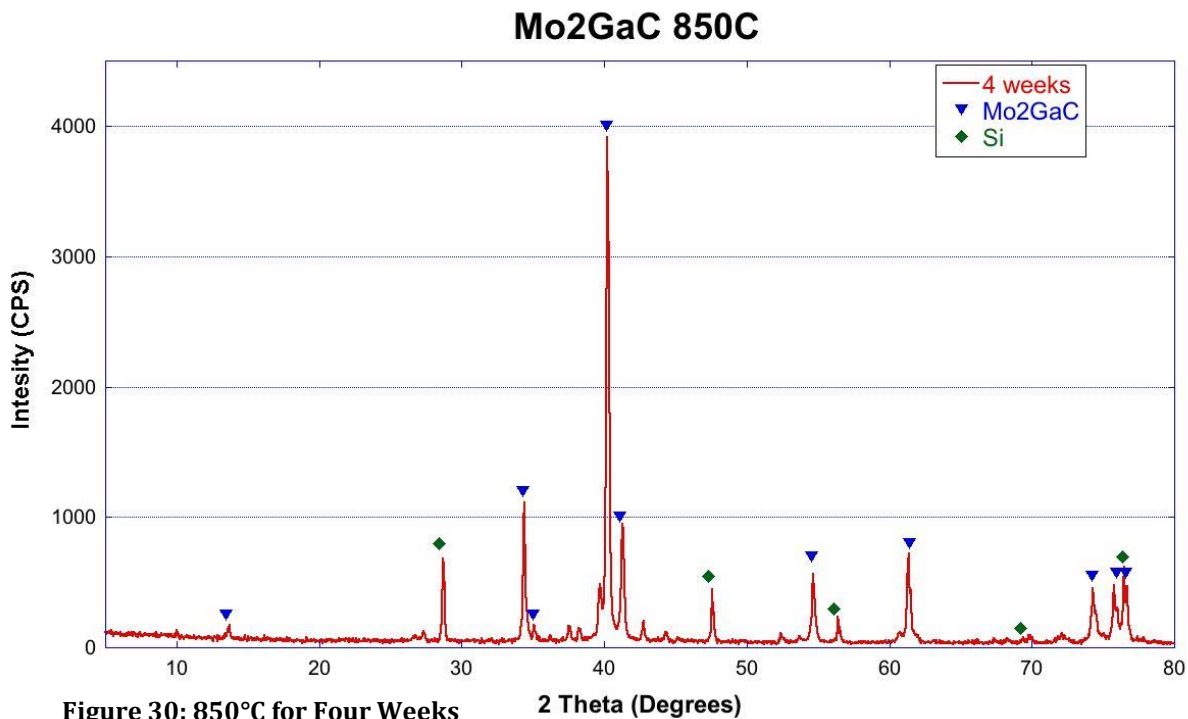


**Figure 28: 850°C for Two Weeks**  
 After two weeks at 850°C Mo<sub>3</sub>Ga was no longer observed, instead Mo<sub>2</sub>C was present. Still, the primary phase was Mo<sub>2</sub>GaC MAX phase



**Figure 29: 850°C for Three Weeks**

The XRD pattern after three weeks looked very similar to the XRD pattern after two weeks. The primary phase is  $\text{Mo}_2\text{GaC}$  MAX phase with a small amount of  $\text{Mo}_2\text{C}$ .

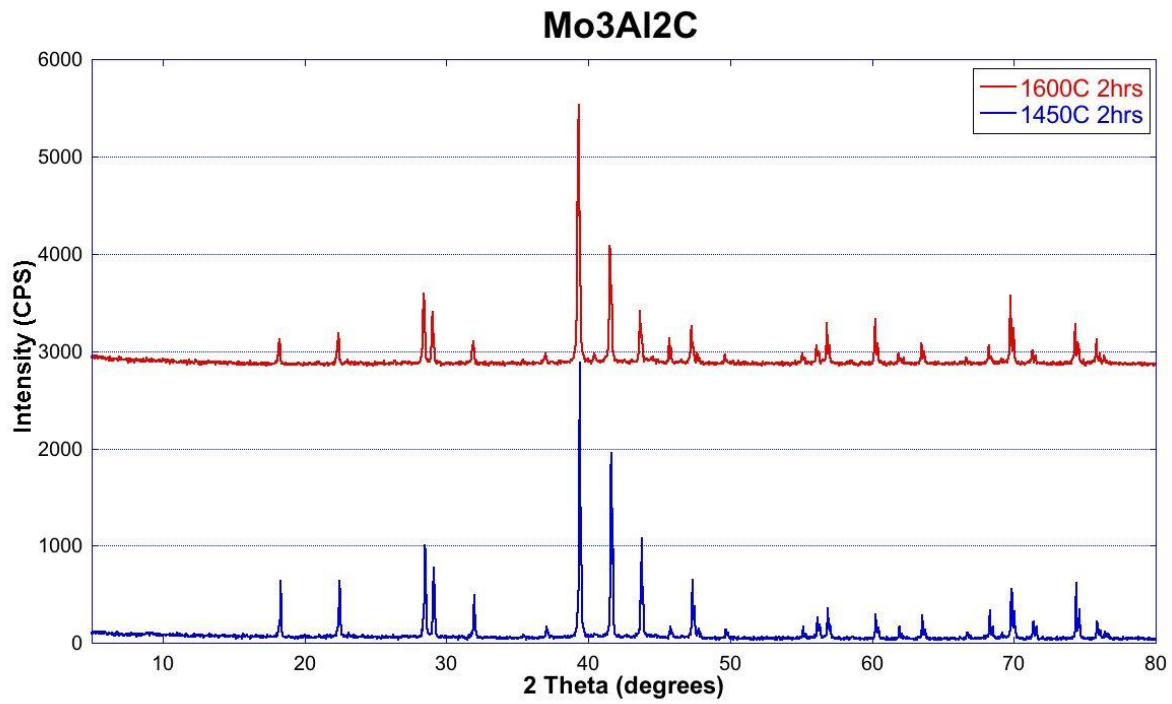


**Figure 30: 850°C for Four Weeks**

After four weeks at 850°C a pure phase of  $\text{Mo}_2\text{GaC}$  MAX phase was synthesized.

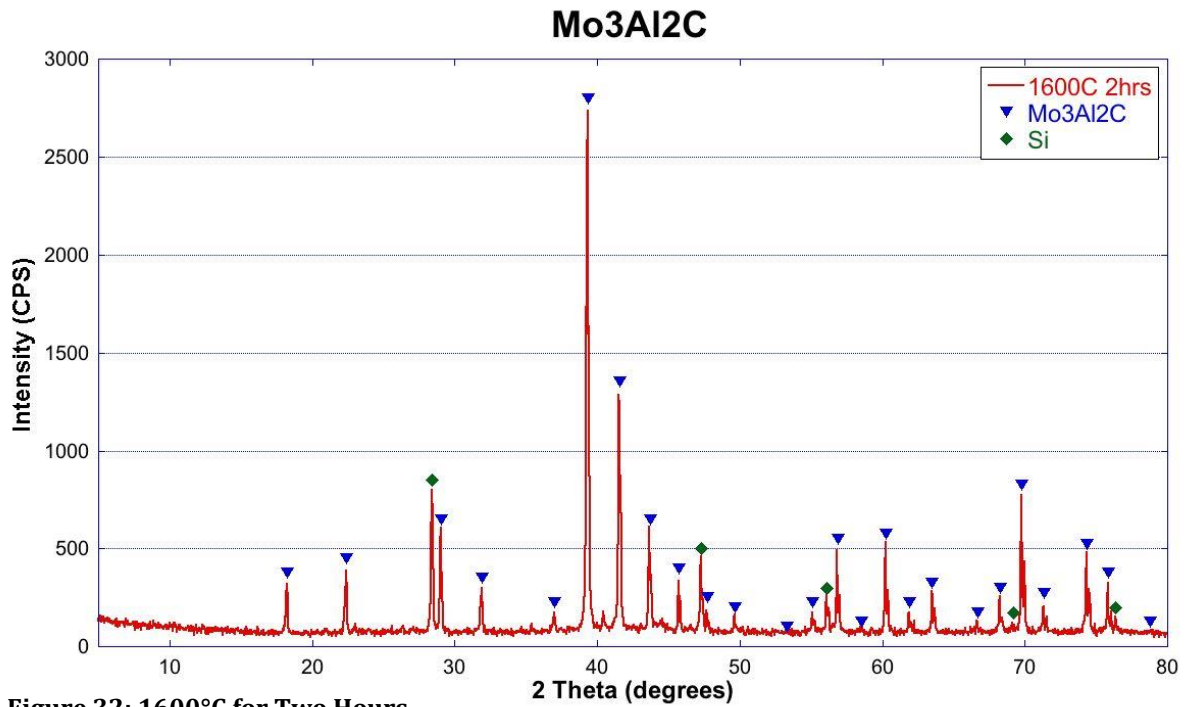
## 8.2 3Mo+2Al+C

The following XRD patterns are of an elemental mixture in a 3:2:1 molar ratio of Mo, Al and C sintered for two hours at 1450°C and 1600°C.



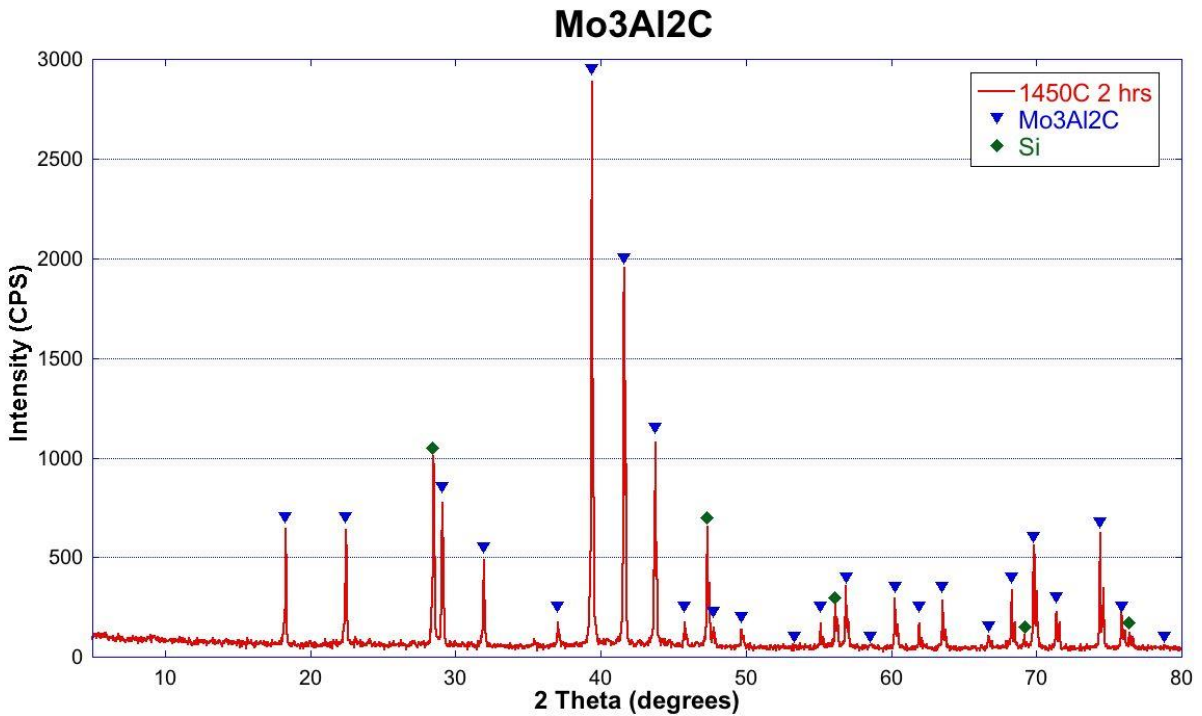
**Figure 31: XRD Comparison**

The two XRD patterns for 1450°C and 1600°C are shown. A pure phase of Mo<sub>3</sub>Al<sub>2</sub>C was produced in both samples.



**Figure 32: 1600°C for Two Hours**

After two hours at 1600°C a pure phase of Mo<sub>3</sub>Al<sub>2</sub>C was synthesized. The adjustment of the elemental mixture to a molar ratio of 3:2:1 Mo:Al:C successfully produced a pure phase.



**Figure 33: 1450°C for Two Hours**

After two hours at 1450°C a pure phase of Mo<sub>3</sub>Al<sub>2</sub>C was synthesized.

## 9.0 Discussion of Secondary Results

### 9.1 2Mo+Ga+C at 850°C

The method used to contain the elemental mixture of Mo, Ga and C in the alumina cylinder and then sealed in an evacuated quartz tube worked extremely well. The molar ration was held constant within the alumina cylinder because all the powder remained within the crucible. This can be seen in figure 34.



**Figure 34: Sample Sealed in Evacuated Quartz Tubing**

The secondary method of sealing the sample within the alumina cylinder was successful. All material was contained within the cylinder.

sample that was sintered in the tube furnace for two hours at both 1450°C and 1600°C. According to the literature a pure phase of this material has not been produced previously [13].

## 10.0 Final Method

### 10.1 Mo<sub>3</sub>Ga+2C

The resulting material from initial experiments from 2Mo+GaN was Mo<sub>3</sub>Ga. This was not the desired material, but was utilized in the following manner. A 3:1:2 molar ratio of elemental Mo:Ga:C was achieved by adding the appropriate amount of carbon to Mo<sub>3</sub>Ga. This powder mixture was ball milled for 24 hours and degassed overnight in a bench top vacuum furnace. This mixture was loaded into an alumina

The XRD patterns clearly showed that Mo<sub>2</sub>GaC MAX phase was produced. The intensity of the corresponding peaks increased from week to week. There was, however, a small percentage of Mo<sub>2</sub>C present in weeks one to three. After four weeks at 850°C a pure phase of Mo<sub>2</sub>GaC MAX phase was synthesized. This was only the second time in history this material was produced.

Also, the first peak in each XRD pattern was unidentified. This small peak corresponds to similar peaks observed in 312 MAX phases. Mo<sub>3</sub>GaC<sub>2</sub> has never been identified. This peak is evidence that a new MAX phase was produced.

### 9.2 3Mo+2Ga+C

After the stoichiometry was adjusted to a 3:2:1 molar ratio of Mo, Ga and C a pure phase of Mo<sub>3</sub>Ga<sub>2</sub>C was produced. This occurred for each

crucible sealed with an alumina disc with cyanoacrylate and weighted with bulk chunk of 312 MAX phase. This was then loaded into a prepared quartz tube and sealed under vacuum. This same method was used previously to successfully seal Mo<sub>2</sub>GaC in quartz tubing. This sealed quartz tubing was then sintered at 850°C for one week.

### **10.2 Densification of Bulk Mo<sub>2</sub>GaC**

Hot Isostatic Pressure (HIP) was used to attempt to fully densify bulk samples of Mo<sub>2</sub>GaC. 20g of powder from the 850°C two week sample was cold pressed into a puck. This puck was loaded into the HIP chamber and surrounded with crushed borosilicate glass. After the chamber was sealed, the temperature was increased above the melting temperature of borosilicate, resulting in liquid borosilicate surrounding the cold pressed puck. This liquid glass was then pressurized with argon gas. In this manner, isostatic pressure and heat densified the cold pressed puck. The sample was loaded to 17ksi at 1000°C and held for eight hours.

### **10.3 MXene from Mo<sub>2</sub>GaC**

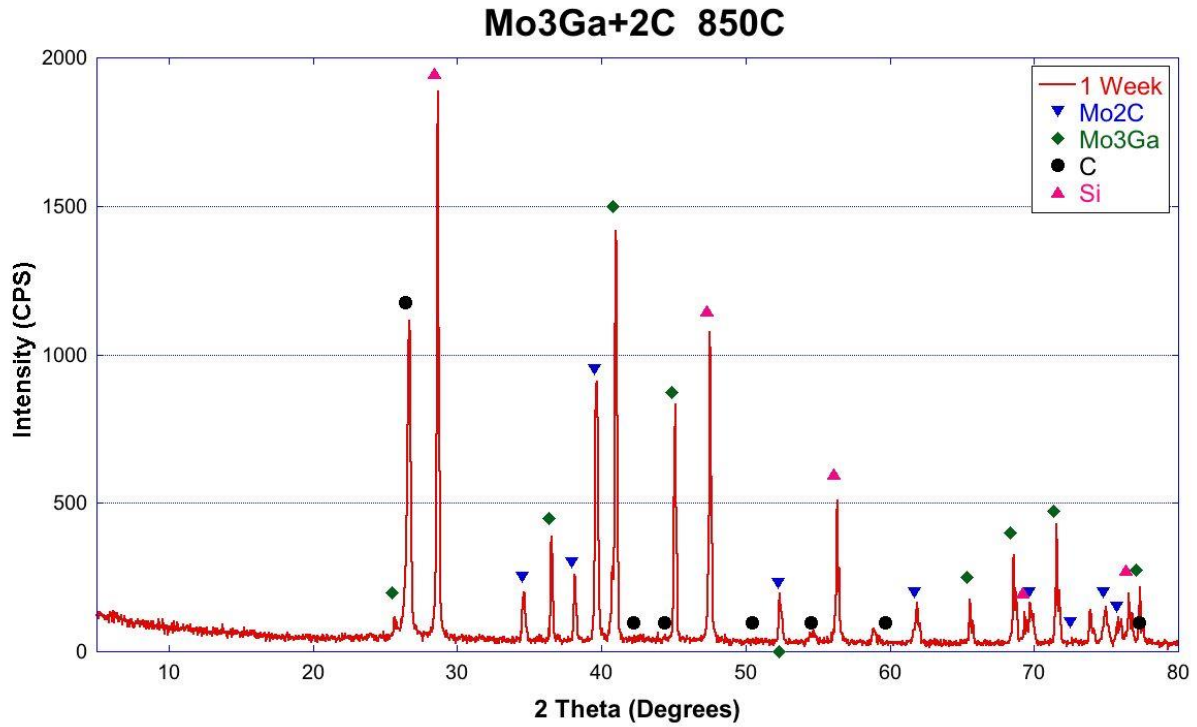
10g of powder from the 850°C three week sample was sifted to 25µm. It was then placed in a HDPE jar and 100mL of 29% concentration hydrofluoric acid was poured on top. A magnetic stir bar was added and the jar placed on a magnetic stirrer for 92 hours. After 92 hours the sample was rinsed ten times with distilled water in a centrifuge until the pH was neutral. Then the sample was rinsed with ethanol and dried overnight in a fume hood.

This same procedure was carried out at a concentration of 50% hydrofluoric acid for 96 hours.



## 11.0 Final Results

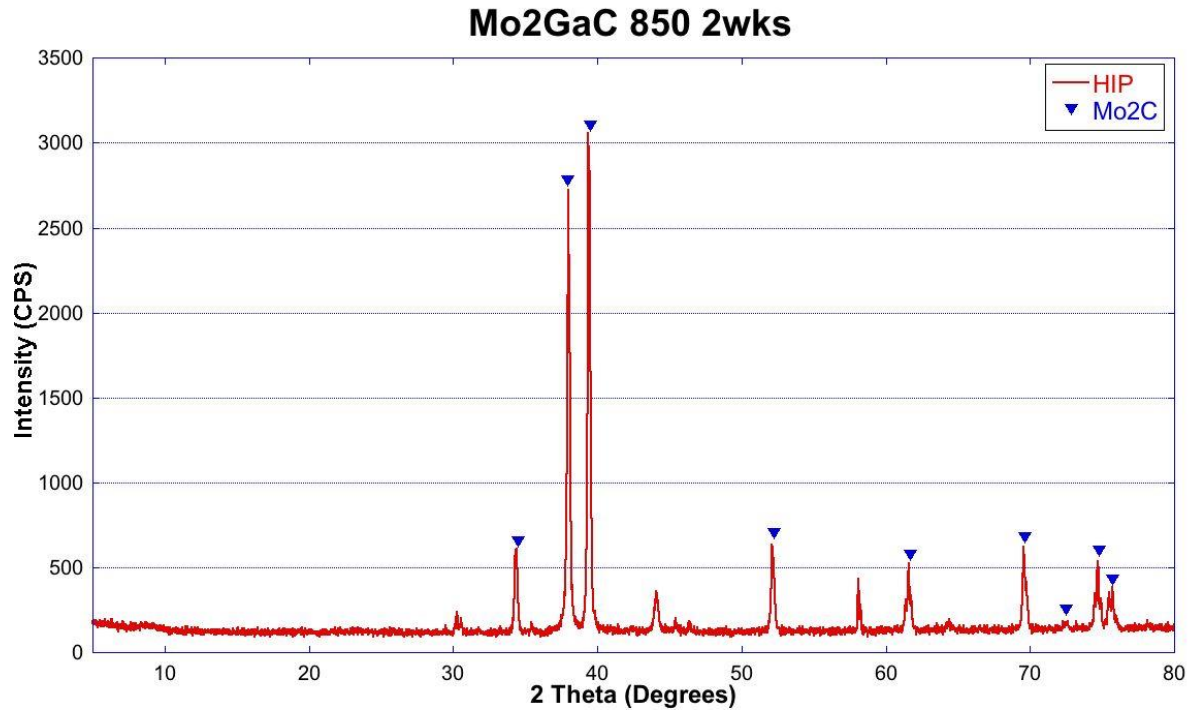
### 11.1 Mo<sub>3</sub>Ga+2C



**Figure 35: Mo<sub>3</sub>Ga+2C 850°C for One Week**

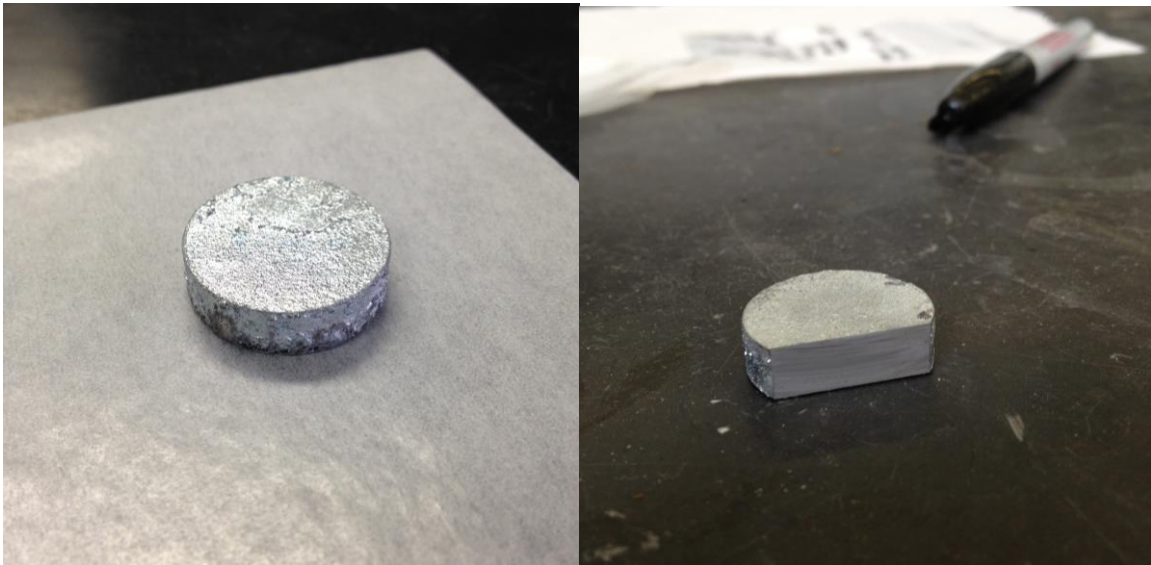
According to XRD, after one week the primary material left was Mo<sub>2</sub>C. Also there was unreacted Mo<sub>3</sub>Ga and C left. Even though the stoichiometry was accurate one week was not enough time for a 312 MAX phase to be produced. Ga seemed to dissociate between 850°C and 1000°C. Therefore the temperature was appropriate, but the time was insufficient.

## 11.2 Densification of Bulk Mo<sub>2</sub>GaC



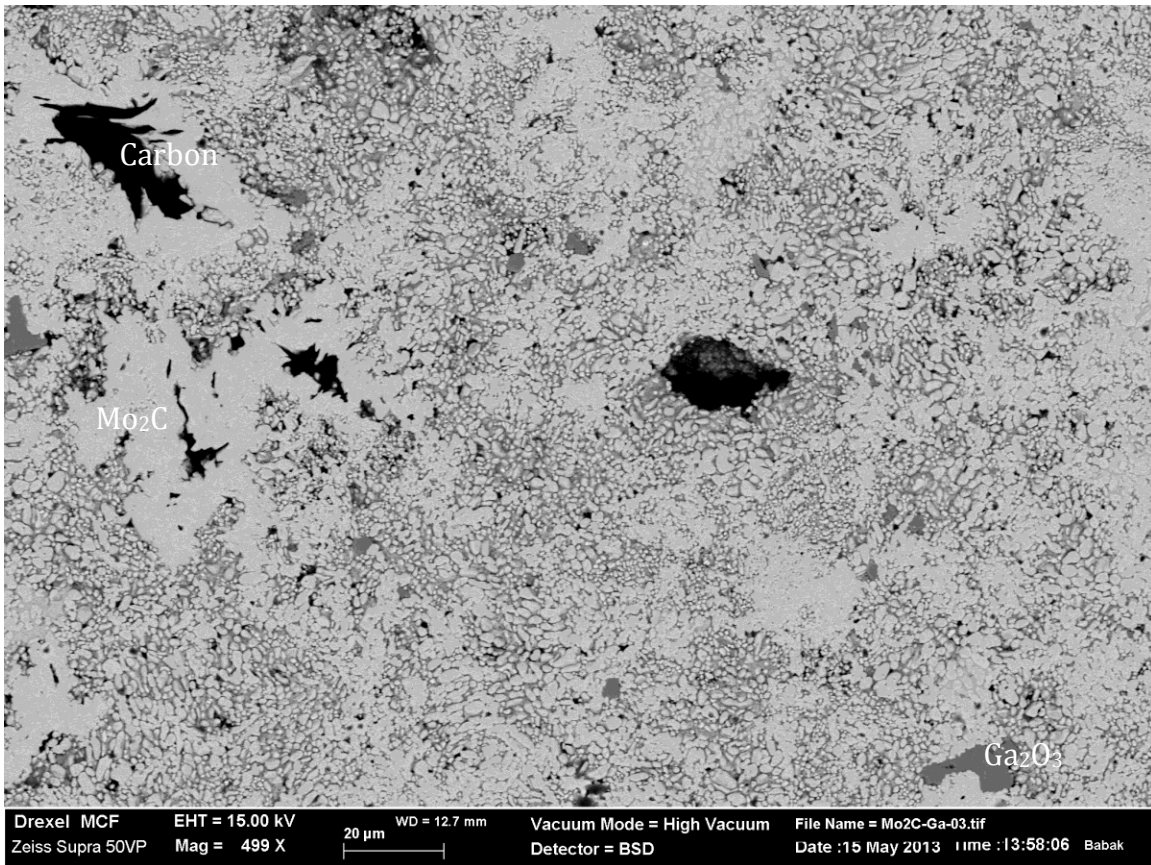
**Figure 36: HIP of Mo<sub>2</sub>GaC 850°C Two Week sample**

Sample was run at 17ksi and 1000°C for eight hours. According to the XRD pattern Ga dissociated somewhere between 850°C and 1000°C. The only material left was Mo<sub>2</sub>C. Either the Ga diffused out of the sample and reacted with the borosilicate glass, or Ga was still in the sample in an amorphous or liquid state, which XRD could not detect.



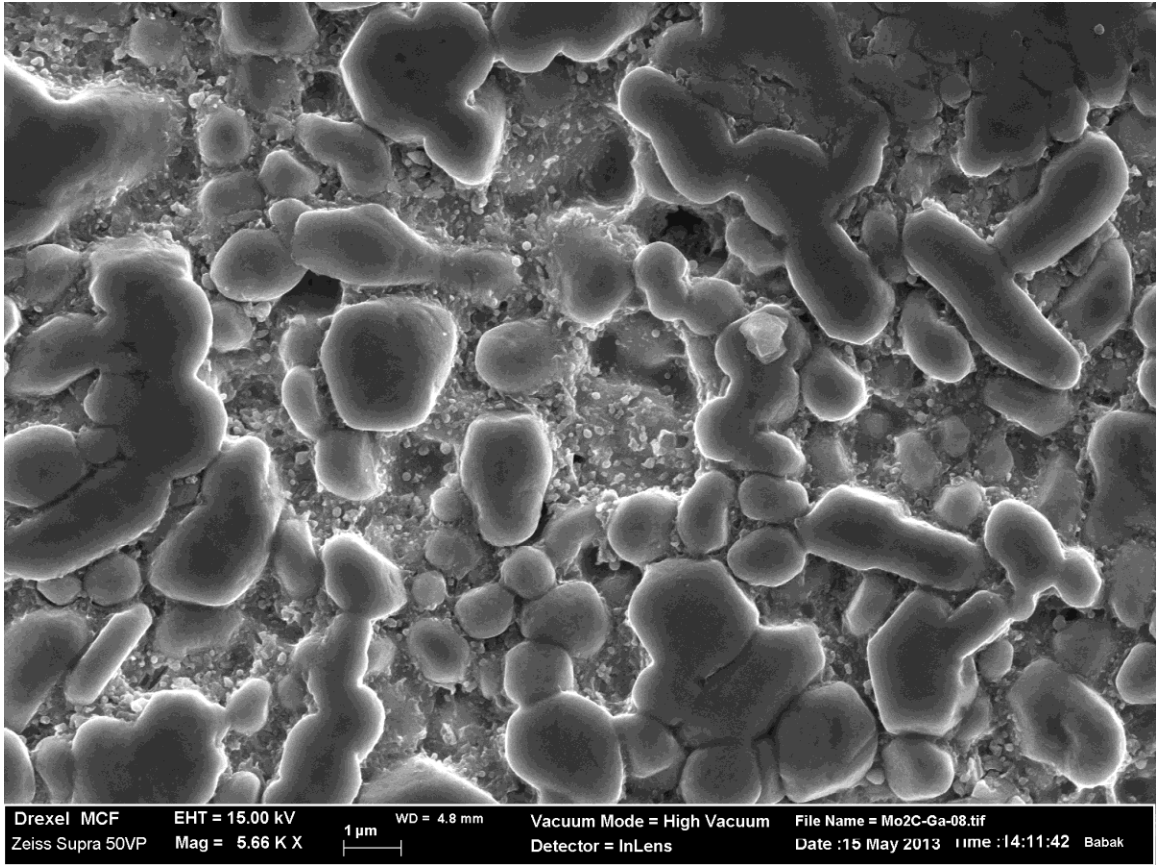
**Figure 37 and 38: Image of Sample after HIP and Cross-section of Sample**

These images show a metallic sheen on both the surface of the sample and the cross section. Visually this showed Ga must be present within the material, contrary to XRD data.



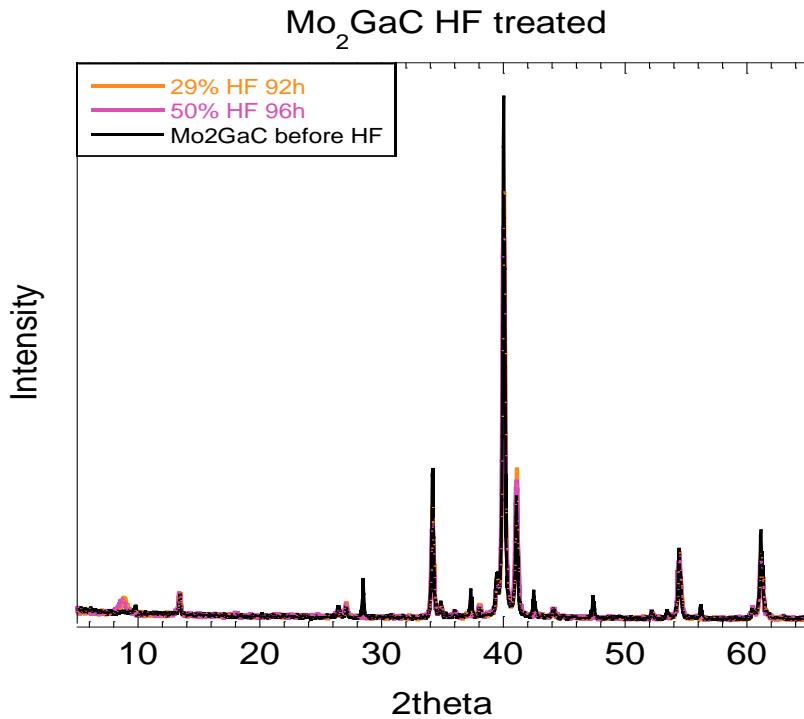
**Figure 39: SEM Image of Mounted and Polished HIP Sample.**

According to EDS C was present as well as Mo<sub>2</sub>C and Ga<sub>2</sub>O<sub>3</sub>. This suggests that there was Ga in the sample after HIP and after it was polished and left in atmosphere it oxidized. Since XRD did not show any gallides or gallium present, gallium must have been in liquid form.



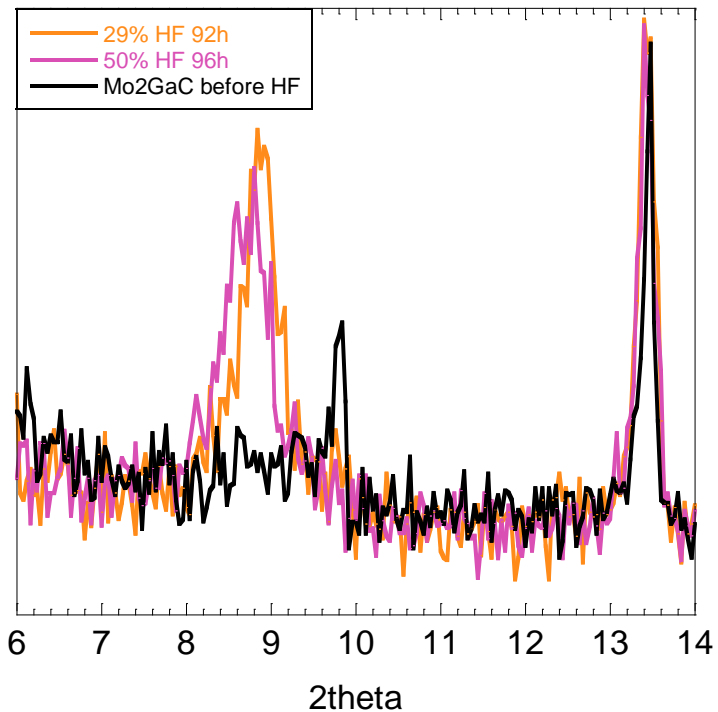
**Figure 40: SEM Image of Mo<sub>2</sub>C particles with Ga and Ga<sub>2</sub>O<sub>3</sub> Between Particles**  
EDS showed these particles to be Mo<sub>2</sub>C, the primary phase observed with XRD.  
However, EDS also showed Ga and Ga<sub>2</sub>O<sub>3</sub> in between the particles.

### 11.3 MXene from Mo<sub>2</sub>GaC



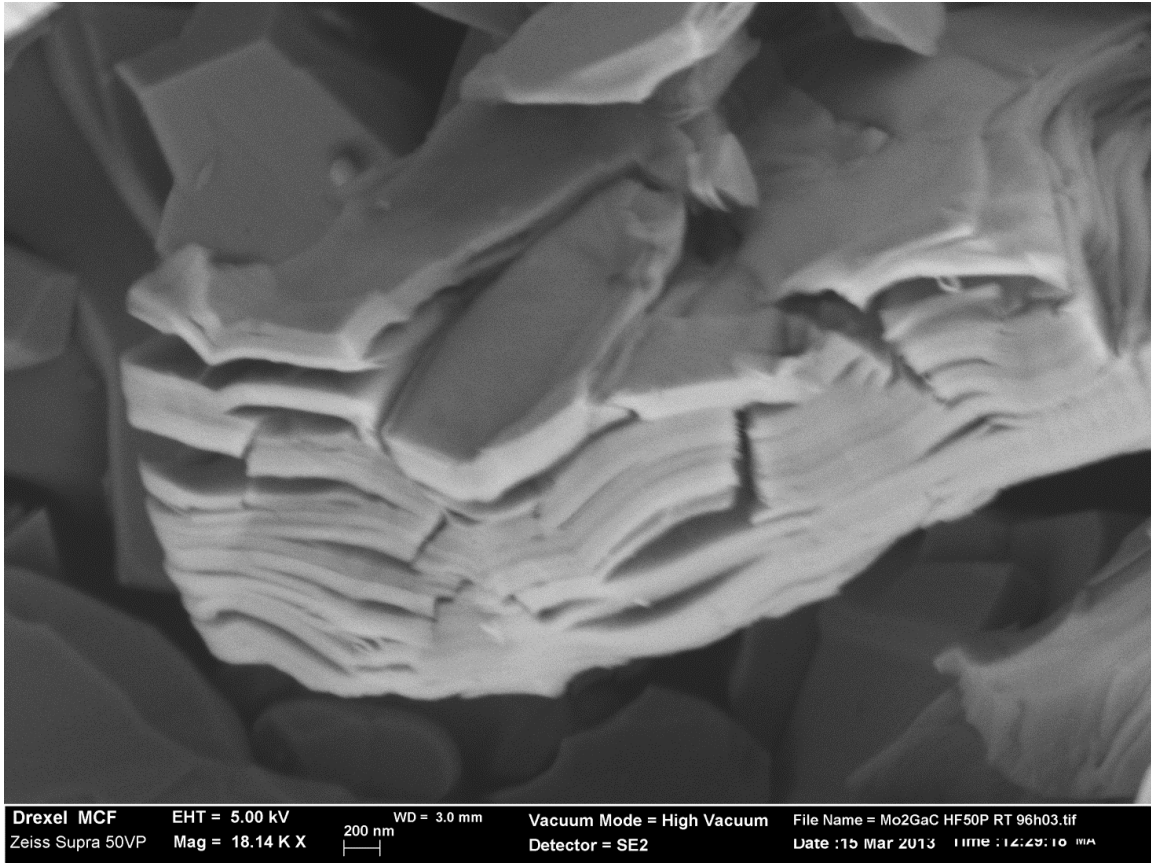
**Figure 41: XRD of Both HF Etched Samples**

These XRD patterns showed excellent correlation between the two treated samples, 29% HF for 92 hours and 50% HF for 96 hours. [Courtesy of Michael Naguib]



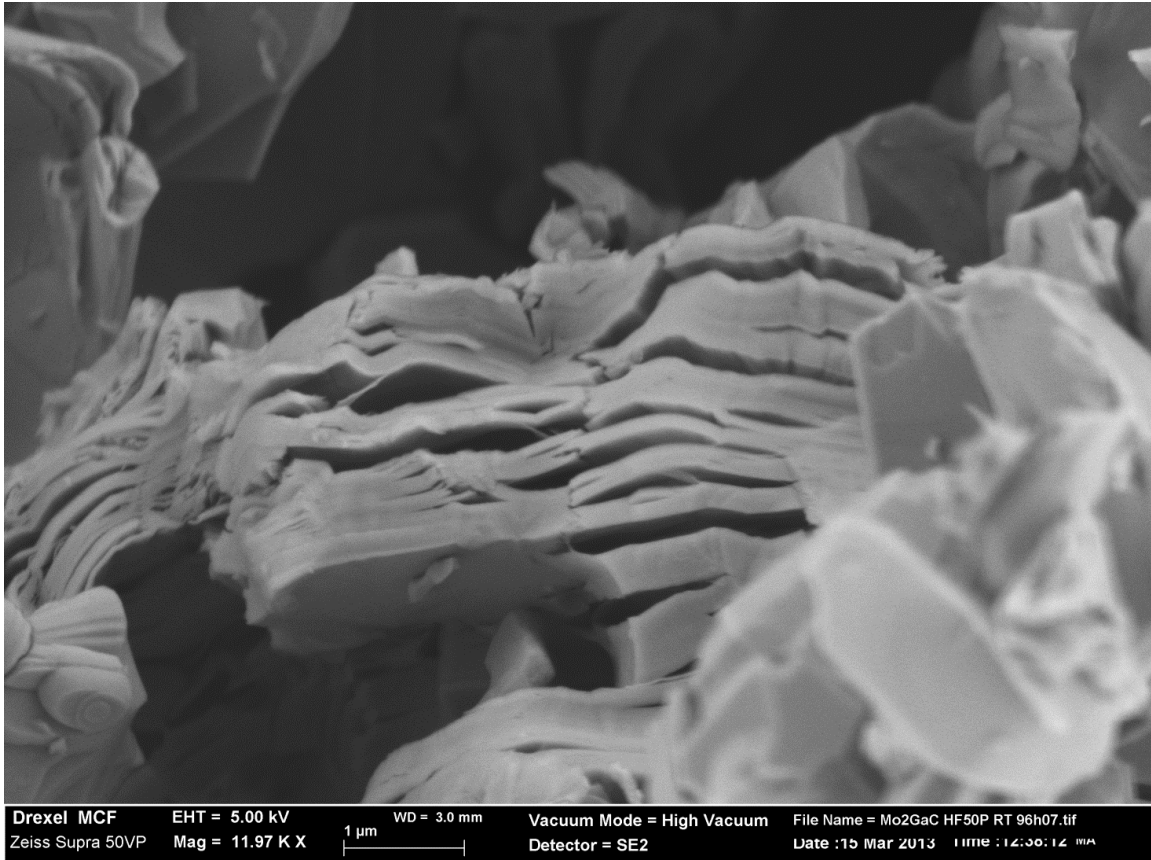
**Figure 42: XRD Patterns Zoomed in on MXene Peaks**

These two peaks correspond to MXene. This data is the same as in Figure 41, just zoomed in on these two peaks to show that MXene was in fact synthesized. [Courtesy of Michael Naquib]



**Figure 43: SEM Image of MXene Flakes**

Several MXene like flakes were observed with SEM. EDS on this flake showed an atomic percent of: 44.46 for C, 12.91 for O, 7.64 for F, 1.26 for Ga and 33.72 for C. This showed that most Ga was successfully etched away with HF acid. [Courtesy of Michael Naguib]



**Figure 44: SEM Image of MXene Flakes**

This is another example of the observed MXene like flakes. The atomic percentage of this flake group was: 28.22 for C, 12.98 for O, 5.08 for F, 0.72 for Ga and 53.00 for Mo. [Courtesy of Michael Naguib]

## 12.0 Discussion of Final Results

### 12.1 Mo<sub>3</sub>Ga+2C

Based on the XRD pattern from the sample held at 850°C for one week the resulting material was primarily Mo<sub>2</sub>C along with unreacted Mo<sub>3</sub>Ga and C. This experiment did not produce any evidence of Mo<sub>3</sub>GaC<sub>2</sub> MAX phase. However, XRD peaks corresponding to 312 MAX phase were observed in the samples of Mo<sub>2</sub>GaC at 850°C for one, two, three and four weeks. There was evidence that Mo<sub>3</sub>GaC<sub>2</sub> MAX phase does exist based on these four samples. This experiment, however, did not allow enough time for the reaction to occur. The temperature was appropriate as gallium tended to dissociate from carbides between 850°C and 1000°C.

## 12.2 Densification of Bulk Mo<sub>2</sub>GaC

A 20g sample of powder from the two week 850°C sample of Mo<sub>2</sub>GaC was cold pressed into a puck and HIP at 17ksi and 1000°C for eight hours. The sample was not fully dense. Density was measured at 7.5 g/cm<sup>3</sup>. Theoretical density of Mo<sub>2</sub>C was 9.1 g/cm<sup>3</sup>. Therefore the sample was only 82% dense.

The resulting material was characterized with XRD and SEM with EDS. The XRD results determined that the only phase present was Mo<sub>2</sub>C. However, based on visual observations there was a metallic coating on the outside of the sample and a metallic sheen observed in the cross section as well. While not empirical, this was evidence that gallium, in some form, was still present within the material.

SEM showed an open porous structure and EDS showed carbon, Mo<sub>2</sub>C and Ga<sub>3</sub>O<sub>2</sub> present. The Ga<sub>3</sub>O<sub>2</sub> occurred after the sample was mounted and polished, exposing the gallium to the atmosphere. Prior to this, during hot isostatic pressing, the gallium dissociated from Mo<sub>2</sub>GaC and migrated to the grain boundaries. Then, during the eight-hour hold, a portion of the gallium diffused along the grain boundaries out of the material and reacted with the borosilicate glass. This is what caused the metallic, gallium layer surrounding the sample. The rest of the gallium remained in the material, at the grain boundaries between the Mo<sub>2</sub>C particles. This was observed in SEM and confirmed with EDS. The reason the gallium was not observed with XRD is that it was in liquid form between the particles of Mo<sub>2</sub>C.

## 12.3 MXene from Mo<sub>2</sub>GaC

After Mo<sub>2</sub>GaC was etched with a 29% concentration of HF acid for 92 hours and also with a 50% concentration of HF acid for 96 hours XRD peaks corresponding to MXene were observed in both materials. In addition SEM confirmed that layers of MXene like flakes were present within the material. Although these flakes were somewhat deformed compared to other MXene's it was shown that gallium could be removed from Mo<sub>2</sub>GaC, leaving a MXene. Further refinement of the etching process is required to produce a higher concentration of Mo<sub>2</sub>C MXene.

## 13.0 Conclusion

### 13.1 Mo<sub>2</sub>GaN

The appropriate thermodynamic conditions were not found to produce a MAX phase of this material. Perhaps a similar method utilized to synthesize Mo<sub>2</sub>GaC would be successful. But due to the high cost of GaN further experimentation was not pursued.

In an attempt to synthesize Mo<sub>3</sub>GaC<sub>2</sub> MAX phase Mo<sub>3</sub>Ga was sintered with carbon at 850°C for one week. The primary phase after one week was Mo<sub>2</sub>C and unreacted Mo<sub>3</sub>Ga with carbon. One week was not enough time to complete this reaction. XRD analysis of Mo<sub>2</sub>GaC at 850°C for one, two, three and four weeks did have peaks corresponding to a 312 MAX phase of Mo<sub>3</sub>GaC<sub>2</sub>.



### **13.2 Mo<sub>2</sub>AlC**

A MAX phase of Mo<sub>2</sub>AlC was not synthesized. Based on what was observed in this project it does not seem likely that this MAX phase is possible. However, a new method of producing aluminum molybdenum carbide has been discovered. Previously this material was sintered at 1500°C in a high vacuum oven for 24 hours with intermittent grinding and compacting and did not result in a pure phase [15]. A pure phase was produced in an inert argon atmosphere at both 1450°C and 1600°C in just two hours.

### **13.3 Mo<sub>2</sub>GaC**

For the second time in history Mo<sub>2</sub>GaC MAX phase was synthesized. A pure phase of this material was synthesized at 850°C for four weeks. The material properties, however, were not characterized. This was a result of not successfully producing a fully dense bulk sample.

An 82% dense sample of Mo<sub>2</sub>C with gallium between the particles of Mo<sub>2</sub>C was produced by hot isostatic pressure of 17ksi and 1000°C for eight hours. The gallium migrated to the grain boundaries and some diffused out of the material, reacting with the borosilicate glass. The rest remained at the grains of the material, between the particles of Mo<sub>2</sub>C. Gallium dissociated somewhere between 850°C and 1000°C. Additional attempts to fully densify bulk samples were not made as a result of the HIP breaking.

Mo<sub>2</sub>GaC was etched with HF acid at concentrations of 29% and 50% for 92 hours and 96 hours respectively. Small MXene peaks were found with XRD after HF treatment. Also, SEM showed some exfoliated particles similar to MXenes. EDS showed a deficiency in gallium on average. EDS of exfoliated particles showed trace amounts of gallium. Based on these results the selective etching of gallium and forming stable Mo<sub>2</sub>C is possible.

## 14.0 References

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## 15.0 Appendices

### 15.1 Budget

<b>PROPOSAL BUDGET:</b>		
<input type="checkbox"/> NSF Career Gr		
<b>TITLE: Synthesis and Characterization of Three New MAX Phases</b>		
Yearly % Increase in Salaries	5%	9/1/12
Fringe Benefit Rate	32.5%	5/31/13
Coop Fringe Benefit Rate	9.7%	8
Indirect Cost Rate	54.5%	
	<b>Year 1</b>	<b>Total</b>
<b>Senior Personnel:</b>		
Principal Investigator ( <i>name</i> ): Dr. Michel Barsoum		
0% (Fall, Winter, Spring) 0.25 Months	42,300	42,300
Research Staff ( <i>name</i> ): Daniel Vryhof	11200	
<b>Senior Personnel Subtotal</b>	<b>53,500</b>	<b>42,300</b>
Part-time Wages (Co-Op Student)	0	0
Fringe Benefits	17,388	17,388
<b>Total Personnel</b>	<b>70,888</b>	<b>70,888</b>
Supplies	2,000	2,000
Purchased Services (SEM, M/C Shop)	600	600
<b>Modified Total Direct Cost</b>	<b>73,488</b>	<b>73,488</b>
<b>Indirect @ 55%</b>	<b>40,051</b>	<b>40,051</b>
Research Assistants ( <i>Tuition</i> ):		
0 (0 month appt. 0 Credits @ \$735/Credits)	0	0
Equipment > \$5,000	0	0
Subcontract > \$25K	0	0
<b>Total Sponsor Funding</b>	<b>113,539</b>	<b>113,539</b>

## 15.2 Constraints

<b>Area of Concern</b>	<b>Discussion</b>
<b>Economic</b>	<b>GaN and Ga are relatively expensive</b>
<b>Environmental</b>	<b>Production of Ga is energy intensive but widely available</b>
<b>Societal</b>	<b>Nothing negative</b>
<b>Political</b>	<b>Nothing negative</b>
<b>Ethical</b>	<b>HF is used to produce Mxene</b>
<b>Health and Safety</b>	<b>HF is used. Also high temperature furnaces.</b>
<b>Manufacturability</b>	<b>Can be scaled up</b>
<b>Sustainability</b>	<b>Ga is extracted from the crude aluminum hydroxide</b>