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得獎獎項 **三等獎**

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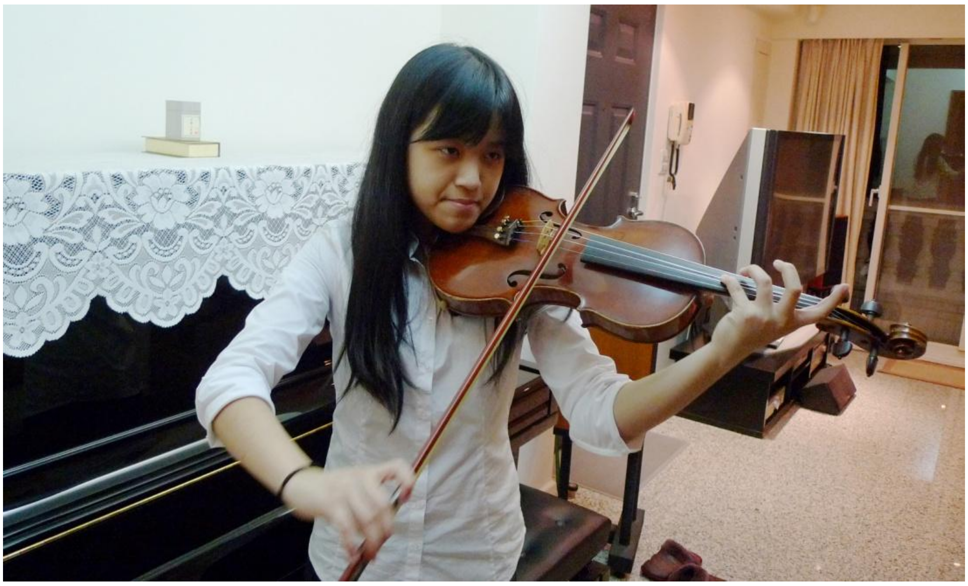
關 鍵 字　超導體、$Bi_4O_4S_3$、$LaOBiS_2$

作者簡介



我是應可歆，目前是非學校型態實驗教育的一員。從小就喜歡排拼圖和解益智玩具，現在則對物理和數學特別感興趣。從 Grade 7 開始在校時就參加了科學與數學的社團，也參加一些競賽和 honor society，看著學長姐們討論著科展內容並透露著濃厚的熱情，不禁也熱血沸騰起來。回到台灣，參加了 2012 年一整年的中央研究院物理所的科學人才培育計畫，讓我能夠持續朝這個目標前進。非常感謝超導實驗室的吳茂昆老師和學長姐們，以及科學人才培育計畫激起了我對科學的熱情並提供了豐富的資源與環境。

摘要

本研究主要探討傾角對面轉變的影響與面轉變的原因。

當柱體由肥皂水中拉起時，泡膜圖形可分為中央膜平行與垂直底面的形式，兩種形式因高的變化而互相轉換的過程稱為面轉變。三到六角柱傾角越大，面轉變時的高越大，反之亦然；六角柱可以面轉變，且在40°到45°之間有臨界角度存在。

本研究以力與能量的角度解釋面轉變‧泡膜藉由改變面積以達到最低的能量、維持穩定狀態，因此本研究計算、比較不同形式的泡膜面積，以解釋面轉變。

我們同時發現三角錐與四角錐都不會發生面轉換；三角錐的實驗值多大於理論值，四角錐的實驗值則多小於理論值。

Abstract

This research mainly explores the effect of tilt on the cylinder of proportion and the reason for the Phase Transition.

When the cylinder is pulled up from the soapy water, the bubble films can be divided into two different modes, films parallel to the center and vertical to the bottom. The Phase Transition occurs when the two forms transform into each other due to different height levels. Some experiments we conducted have concluded that different prisms being pulled with different tilts affect the height of the Phase Transition. The larger the tilt from the triangular to hexagonal prism turns, the bigger the height value of the Phase Transition becomes, vice versa. We also found that hexagonal prism can perform the Phase Transition, with a critical angle between angle forty to forty-five.

Our research is focused on interpreting the force- and energy-based Phase Transition. The bubble films can be energy-low and stable through area proportions. Hence, we calculate and compare different proportions of bubble films to interpret the Phase Transition.

Also, we have found that the triangular pyramid and the square based pyramid do not perform the Phase transition. Additionally, the experimental value of the triangular pyramid is bigger than its theoretical value, more often than not; the experimental value of the square based pyramid, mostly smaller than its theoretical value.

壹、 前言

Kamerlingh Onnes 經由化學元素汞在 1910 年代時發現了超導。當他把汞降溫時，發現汞的電阻率竟然在低溫度時變得完全沒電阻。在這個巨大的發現之後，出現了一個一直持續幾十年的問題。不同的超導體一直沒有如預期的提升轉變溫度 (T_c)，Nb_3Ge 的 23KT_c 曾在 1873 後年成為了 T_c 最高化合物。

發現了超導層如氧化銅礦後引進高-T_c 超導體。現在可以說我們有兩種類型的高-T_c 超導體、 銅氧化物超導體和鐵基超導體。層狀晶體結構或更籠統的說低維超導體可能就是讓銅氧化物及鐵基超導體擁有高 T_c 的原因。

今年 7 月時發表了新的超導材料， $Bi_4O_4S_3$。其晶體結構表示 $Bi_4O_4S_3$ 具有層狀晶體結構，並且很可能是高-T_c 超導體。新類型的層狀超導體開闢了物理和化學的低維超導體中的新領域。

貳、 研究動機

今年能夠有機會參觀研究機構的實驗室。當我在超導實驗室並且學到有關超導的新知識後，我便開始對超導有很大的興趣。最吸引我的就是如果能尋找到室溫超導，就能夠解決現代人類最困擾的能源問題，並且單單談能夠在傳遞過程中沒有消耗掉任何電就可以達到最好的節約效果了。於是開始看許多論文及期刊有關最新的超導訊息就發現了 BiS_2 超導層和低維度層狀超導體。除了覺得非常有趣之外，看到和研究超導的最新研究就足以讓我熱血沸騰了。所以我打算以不同的製程方式來分析及探討具有 BiS_2 超導層的 $Bi_4O_4S_3$ 的超導性質。

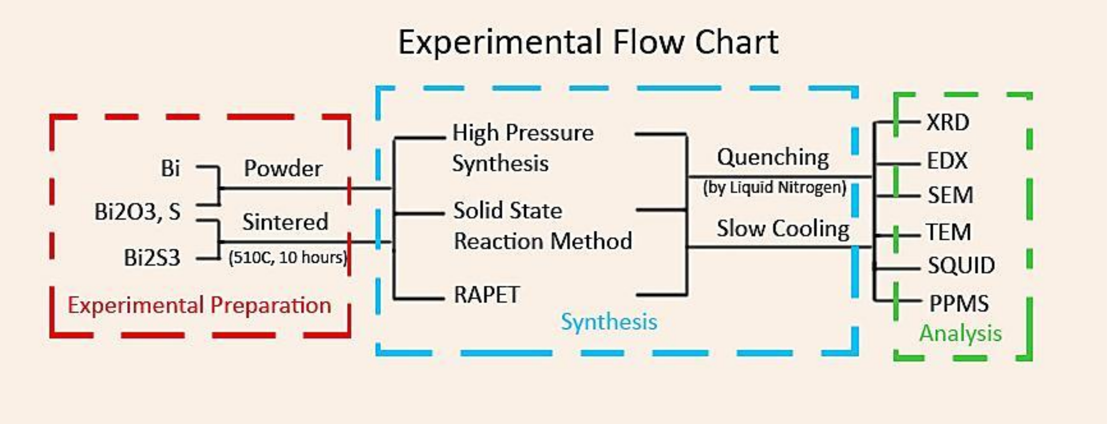
參、 研究目的

一、用不同的製程方式以及不同的條件如溫度，壓力，降溫方式等

來提高 BiS_2 超導層的臨界溫度(T_c)以及超導比例。

二、從化合物以及結構上探討不同條件下升高 T_c 的原因。

下圖是整個實驗的流程圖，從準備、合成到分析的研究流程。開始時選用兩種方式配出 $Bi_4O_4S_3$,再 來選擇三種合成方式，高壓合成，固態合成，以及 RAPET。取出樣品的過程通過兩種冷卻方式，淬火以及緩慢冷卻。最後使用六種分析儀器，SQUID（超導量子干涉儀），XRD（X 光繞射儀），PPMS（物理性質測量系統），EDX（X 光能量分析儀），SEM（掃描式電子顯微鏡），TEM（穿透式電子顯微鏡）來分析樣品。



肆、 研究設備及器材

一、合成實驗

(一)高壓合成法, TRYCA 350 SANKYO

(二)固態合成法

(三)RAPET Method (Reactions under Autogenic Pressure at Elevated Temperature)

二、分析實驗

(一)XRD (X 光繞射儀), PANalytical X'Pert X-ray Diffraction

(二)EDX (能量色散 X 射線儀)

(三)SEM (掃描式電子顯微鏡)

(四)TEM (穿透式電子顯微鏡)

(五)SQUID (超導量子干涉磁量儀) Quantum Design

(六)(PMS (物理性質量測系統), Quantum Design model 6000

伍、 實驗製備

一、粉末製備

化學名稱	縮寫	廠商
鉍粉	Bi	Alfa Aesar
氧化鉍	Bi_2O_3	Cerac
硫	S	Riedel-deHaen
硫化鉍(III)	Bi_2S_3	自製
碲化鉍(III)	Bi_2Te_3	Alfa Aesar
硒化鉍(III)	Bi_2Se_3	Alfa Aesar

化學反應式

$Bi_4O_4S_3$ 粉末：

$4Bi_2O_3 + 4Bi + 9S \rightarrow 3\ Bi_4O_4S_3$

$Bi_4O_4S_3$ 一次燒結礦：

$Bi_2S_3 + 4Bi_2O_3 + 3S \rightarrow 3Bi_4O_4S_3$

$Bi_4Te_4S_3$ 粉末：

$4Bi_2Te_3 + 4Bi + 9S \rightarrow 3Bi_4Te_4S_3$

$Bi_4Se_4S_3$ **粉末**：

$4Bi_2Se_3 + 4Bi + 9S \rightarrow 3Bi_4Se_4S_3$

二、實驗製備

(一)轉換分子量和計算每一種化學品的適當重量。

(二)充分混合粉末。

(三)(定合成方法和商業粉末製備的同時保持準備一次燒結 Bi2S3 粉研磨後的其他條件。

(四)壓縮的對流的粉成錠和固態反應方法的 510 度 10 小時為粉末燒結 Bi2S3 準備條件作好準備。

三、冷卻過程

(一)緩慢冷卻

1. 等到樣本自然冷卻。

(二)淬火

1. 準備液態氮、燒杯和夾具。
2. 將樣品放入燒杯和燒杯拾取固定夾,並將一半燒杯放入液態氮。

陸、 研究方法或過程

一、固態燒結法

(一)固態燒結法的簡要說明

固態燒結法是最傳統的製程方式。這種方式可以製程金屬氧化物，硫化物和其它類型的材料且製備大量的化合物。唯一需要的封管機和加熱器，這比高壓合成或RAPET更容易合成。和其它方法比較如高壓合成，固態燒結法的樣品的量會大的多。雖然態燒結法在整個樣品的製作過程需要較長的時間，但它確定一些條件後才會是最有利的。

(二)儀器和材料

1. 石英管
2. 封口機
3. 加熱器

(三)實驗步驟

1. 計算 2 g 的 Bi4O4S3 且使用高純化學製品配製。
2. 用瑪瑙研缽研磨化學製品。
3. 用油壓機持壓 15 分鐘，3 噸。
4. 用封管機抽管內真空到 10-6 Torr 後封管。
5. 把封好的管子放入加熱機內設定溫度程序後開始固態合成法

二、高壓合成法

(一)高壓合成法的簡要說明

高壓合成方法在探索新的材料比其他方法更有利。這方式可以縮短樣品合成的過程，以便找出適合的材料的條件所需的時間。材料通過壓縮的化合物可以增加的穩定性，更小的體積和增加其密度。高壓合成方法還可以防止有毒元素的蒸發。

高壓合成方法一直對於高溫超導的發現和多層超導體非常有利。因此，高壓合成為新材料在確定的時間，溫度，壓力條件時是個不錯的選擇。

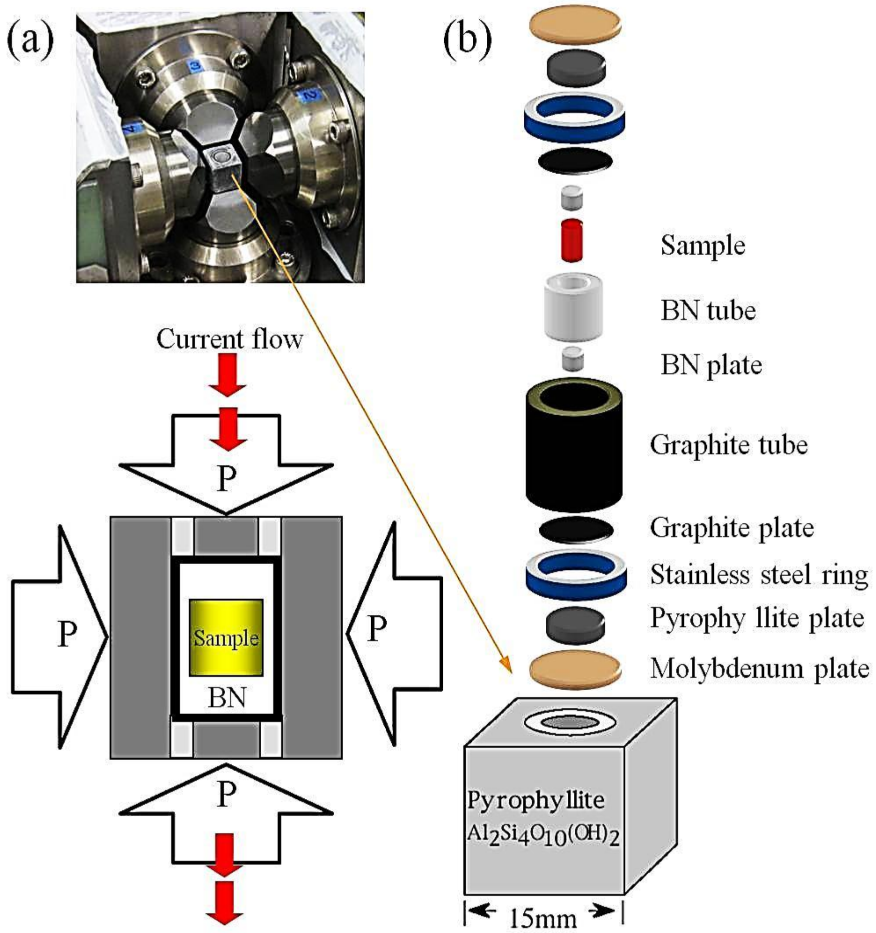
(二)儀器和材料

1. TRYCA 350 SANKYO
2. 硼氮化粉

3. 石墨管和石磨片
4. 不銹鋼圈
5. 葉蠟石板和立方體（Al2Si4O10(OH)2)

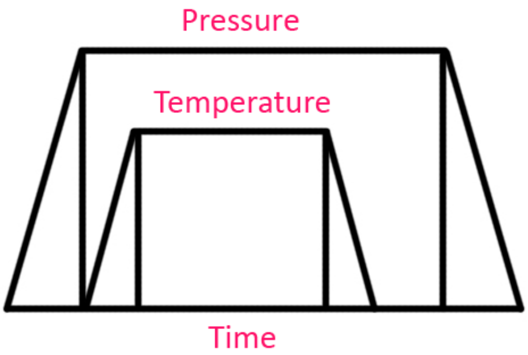
（三）實驗步驟

1. 計算 Bi4O4S3 劑量比使用高純化學製品配製。
2. 用瑪瑙研缽研磨化學製品。
3. 壓縮 0.36 g 的 Bi4O4S3 成適當大小的顆粒，封裝到氮化硼管和板組成的封閉容器。
4. 以下圖的方式把所有材料組裝成一個小方塊。
5. 確認所有材料無異狀，無凸出下陷。



6. 把方塊放入高壓機裡。

7. 調整的高壓力器具，參考下圖片做程式的溫度和壓力設定。
8. 按下啟動壓力的按鈕高壓力器具向上頂起樣品，然後運行壓力程式。
9. 手動微調壓力變化 （8 毫升/分），當達到目標壓力時，然後按向樣品施加壓力的按鈕。



三、RAPET（Reactions under Autogenic Pressure at Elevated Temperature）

(一)RAPET 簡要說明

RAPET 方法是一種特殊的製程方式，可用來製造納米等級的樣品。

與高壓合成或固態燒結法不一樣的是樣品大多呈粉狀。這可能會導致的困難做分析，如物理性質測量系統（PPMS）就無法量測粉狀樣品。雖然它是粉末狀的，但它是一個快速和方便的方法。它也可以像高壓合成法一樣被用來作為一個測試條件的方法。由於比較少人會用這種製程樣品的方法，它使 RAPET 成為一個較稀有且好用的方法。

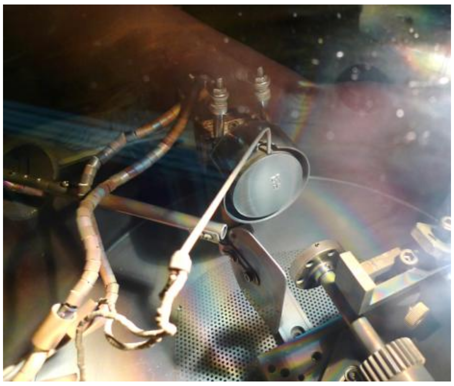
(二)儀器和材料

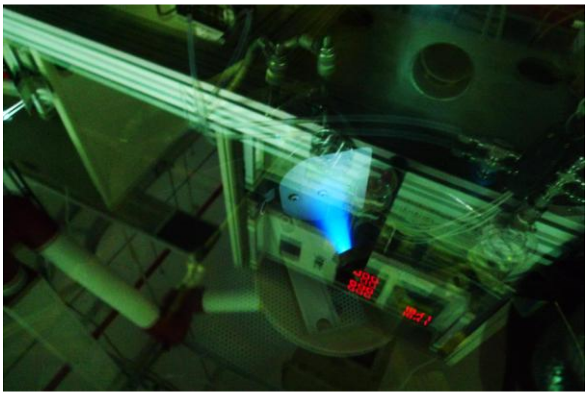
1. RAPET 管狀加熱器
2. 雙頭鎖

(三)實驗步驟

1. 計算 2 g 的 Bi4O4S3 且使用高純化學製品配製
2. 用瑪瑙研缽研磨化學品。
3. 將化學品放入雙頭鎖，然後鎖緊雙頭鎖緊。
4. 將雙頭鎖放入管狀加熱器，開啓加熱器。
5. 栓緊所有紐後大開抽真空的馬達後分段式抽真空。
6. 一旦壓力錶達到完全真空，打開氬氣。
7. 開啓氣體流動按鈕，並相應地調整氣體流量的量。
8. 旋開加熱器末端的旋紐後使得氬氣流通。
9. 手動設定程式的時間和溫度。

四、 雷射鍍膜（Pulsed Laser Deposition）





（一）PLD 簡要說明

雷射鍍膜是用一個高功率脈衝激光束聚焦到一個點入真空室內，打上靶材。這種材料將被汽化從靶材鍍到矽晶片基板上。

（二）儀器和材料

1. PLD 儀器

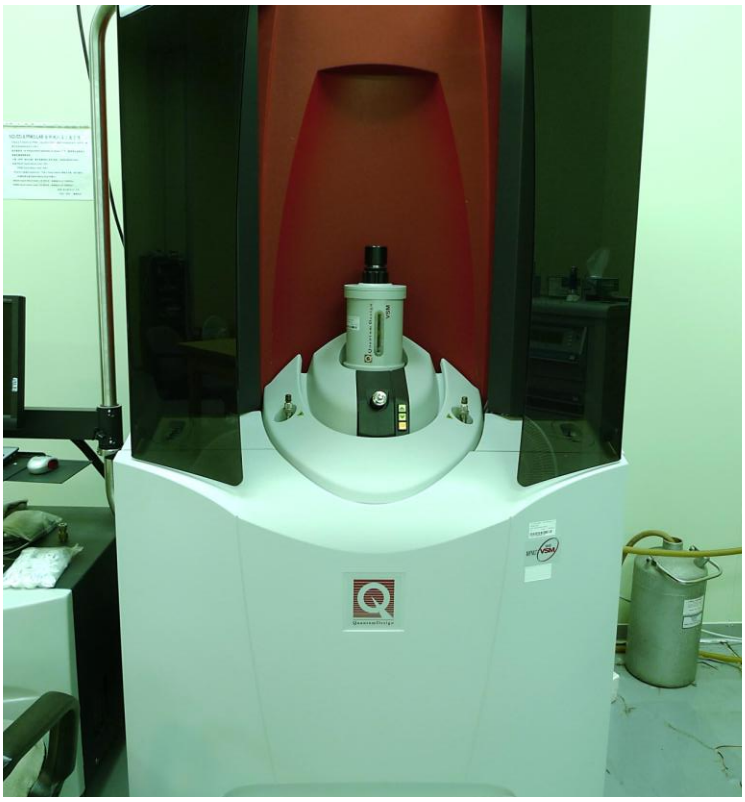
（三）實驗步驟

1. 放上靶材，調整聚焦

2. 開啓 PLD

柒、　分析方法

一、 SQUID （超導量子干涉儀)



(一) SQUID 簡要說明

超導量子干涉儀是利用超導量子干涉元件(SQUID)結合了電子、機械、低溫、真空等技術來量測磁化率的精密儀器，SQUID 是目前所發現最靈敏的磁感應元件，故它最適合微小磁化率的感測，其應用範圍主要是化學、物理材料磁化率的量測。

(二) 實驗方法

1. 將少量粉末樣品放入樣品塑膠膠囊。
2. 顯示溫度為 300 K 與 0Oe 的磁場，將樣品插入 SQUID。
3. 按下按鈕兩次。
4. 檢視檢測點。

5. 開始 15 K/min，從 300 K 到 10 K 及 3 K/min 從 10 K 到 2 K 的溫度冷卻。
6. 到 2 K，加 10Oe 並測量 4 秒/點 至 15 K。
7. 啟動 FC 以同樣的速度從 15 K 到 2 K。

二、XRD（X 光繞射儀)

(一)XRD 簡要說明

X-光繞射(X-ray diffraction)是最常見用來決定固體晶體結構的工具，繞射發生於當光束被一規則排列點或線的散射，散射後的同相光產生建設性干涉，相異相光產生破壞性干涉。它提供不同角度光束的強度資料，能夠做結構間的比對、估計結構的晶格係數、甚至經由精算相似結構間的晶格係數變化而解析出結構中原子的排列。

（一）實驗方法

1. 將樣品磨成粉，將其放在繞射板。

2. 將有粉末樣品的繞射板插入到 XRD。

3. 設置繞射角度 10 度到 80 度並開始檢測。

三、PPMS（物理性質測量系統）

（一）PPMS 簡要說明

PPMS 系統由一個主機和各種應用測量的模組化元件構成。主機提供了一個強磁場（超導磁體）和極低溫的環境（液氦溫度範圍），根據研究需要測量各種物理性質。

（二）實驗方法

1. 準備樣品，用銀膠連接四條鉑金線。
2. 將其插入到物理性質測量系統。

四、X 光能量分析儀 EDX (Energy-dispersive X-ray spectroscopy)

EDX 的分析技術用於尋找樣品的化學表徵。當我們有 EDX 數據時，它會示出 Bi，O，和 S 的質量百分比。EDX 使用一些 X 射線激發來檢查樣品。它會發射的帶電粒子到樣品上。因此，我們能夠知道究竟是什麼和樣品中的百分比，來檢查是否化合物的比例依然正確。

五、掃描式電子顯微鏡 SEM (Scanning Electron Microscope)

掃描式電子顯微鏡是用聚焦電子束在試樣表面逐點掃描成像，由聚焦的電子束掃描產生的樣品的圖像。所產生的圖像通常以微米單位計算。

六、穿透式電子顯微鏡 TEM (Transmission Electron Microscopy)

穿透式電子顯微鏡具有極高的穿透能力及高解析度，透過電子束通過極薄的樣本看到極小，達奈米等級的圖像。

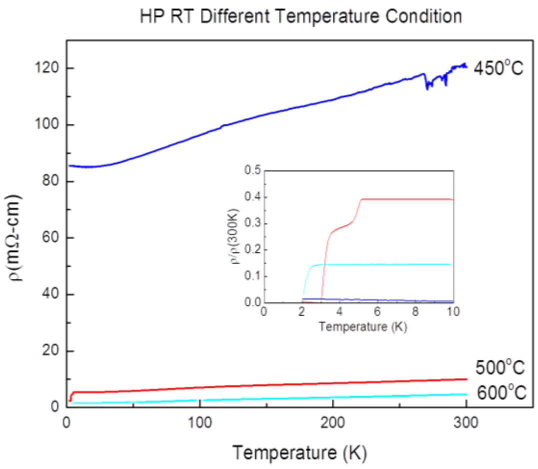
捌、 研究結果與討論

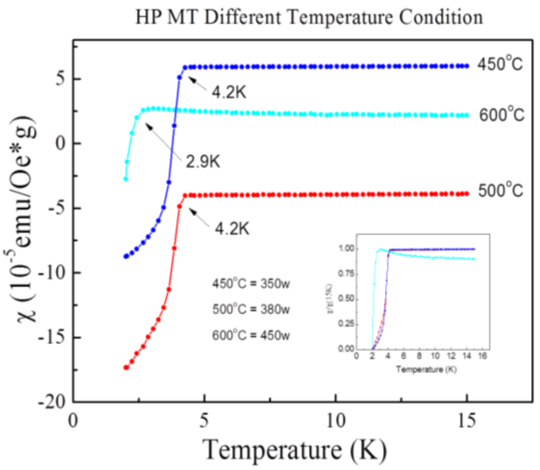
一、樣本條件分析

(一)溫度條件

我選擇高壓合成法作為起始實驗的合成方法，因為對於新材料來說這個方法是個非常有效能夠找到反應時間、溫度等條件的方法。經由閱讀最近發表的 $Bi_4O_4S_3$ 固態燒結法的論文設定起始溫度約 500 度。由於尚未有任何論文運用高壓合成法，所以暫且先用固態燒結法的起始溫度當作實驗的起始溫度。我測試了三種不同的溫度條件，從 450 到 600 度之間來檢查 500 度是否為適當的合成溫度。分析結果由 SQUID 和 PPMS 來斷定。

						SQUID		PPMS
Name	Method	Condition	Cooling Con	Temp deg C	Hold Time (Hr)	Tc (K)	Mag. Sus.	Resistiv (mohm-cm)
HBOS1	HP	Powder	Slow Cooling	600	2	2.9	10^-5	1.05
HBOS2	HP	Powder	Slow Cooling	500	1	4.2	10^-5	2.97
HBOS3	HP	Powder	Slow Cooling	450	1	4.2	10^-5	85.1





通過上面的實驗結果，可以斷定 T_c 大約是 4.2K 而磁化率是 10^{-5}。我們能找到的唯一的改變是從生產和加工方法，最低的電阻率是 1.05，但其 T_c 是比其他人低得多。因此，高 T_c 和第二低的電阻率是最佳的選

擇，就是溫度攝氏 500 度的反應條件。

上方的兩個圖，一個是磁化率，一個是電阻率。在左邊的圖中，由 SQUID 資料顯示 450 和 500 度資料比 600 度的有更好的超導百分比。右圖顯示了 500 度樣品有最快的降幅的電阻率，更接近為零電阻率，並有最大的 T_c 從 PPMS 的資料來看。

因此選擇攝氏 500 度左右的溫度條件，再繼續比較不同化學條件和冷卻條件。

(二)化學條件

有兩種方式準備 Bi4O4S3 ，商業粉末方式與一次燒結 Bi2S3 的方式。經由論文顯示，一次燒結的 Bi2S3 增加了鉍氧化物的超導性。因此，Bi4O4S3 的三種合成方法，高壓合成法、固態燒結法和 RAPET 以商業粉末與一次燒結 Bi2S3 的不同方式來作比較。

Bi2S3 的一次燒結以適當比例的鉍粉和硫磺粉，使用固態燒結法，在 510 攝氏度持續 10 小時。

$Bi_4O_4S_3$ 化學反應:

商業粉末：

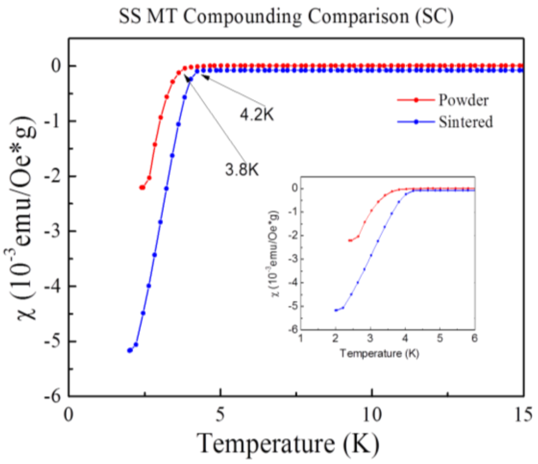
$4Bi_2O_3 + 4Bi + 9S \rightarrow 3Bi_4O_4S_3$

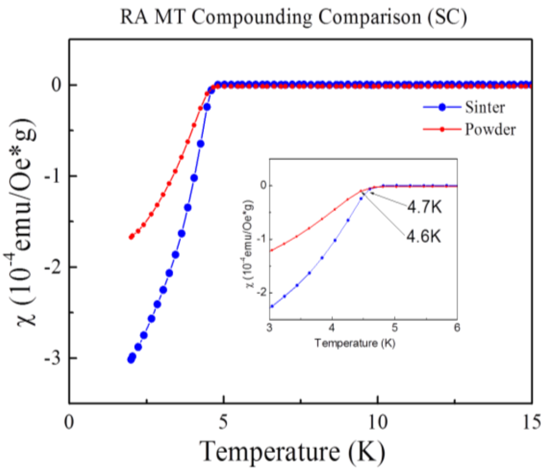
一次燒結的 Bi_2S_3:

$Bi_2S_3 + 4Bi_2O_3 + 3S \rightarrow 3Bi_4O_4S_3$

在下面的圖表上顯示三個不同的方法比較。

					SQUID	
Method	Condition	Cooling Con	Temp deg C	Hold Time (Hr)	Tc (K)	Mag. Sus.
HP	Sintered	Slow Cooling	500	1	4.2	10^-5
HP	Powder	Slow Cooling	500	1	4.2	10^-5
HP	Sintered	Quenching	500	1	4.1	10^-5
HP	Powder	Quenching	500	1	4.2	10^-4
SS	Sintered	Slow Cooling	510	10	4.2	10^-3
SS	Powder	Slow Cooling	510	10	3.8	10^-3
SS	Sintered	Quenching	510	10	4.7	10^-2
SS	Powder	Quenching	510	10	4.7	10^-2
RAPET	Sintered	Slow Cooling	510	10	4.7	10^-4
RAPET	Powder	Slow Cooling	510	10	4.6	10^-5
RAPET	Sintered	Quenching	510	10	5.03	10^-4
RAPET	Powder	Quenching	510	10	5.03	10^-4





1. 高壓合成法：

高壓合成樣品有相近的 T_c ，儘管差異的混煉條件 (燒結或粉末)。高壓合成的樣本顯示，T_c 約 4.2 K，而磁化率大約 10^{-4}。雖然我們能夠概括其 T_c 和磁化率，但我們都是不能確定趨勢必須進一步在化學分析由 EDX 討論。

2. 固態燒結法：

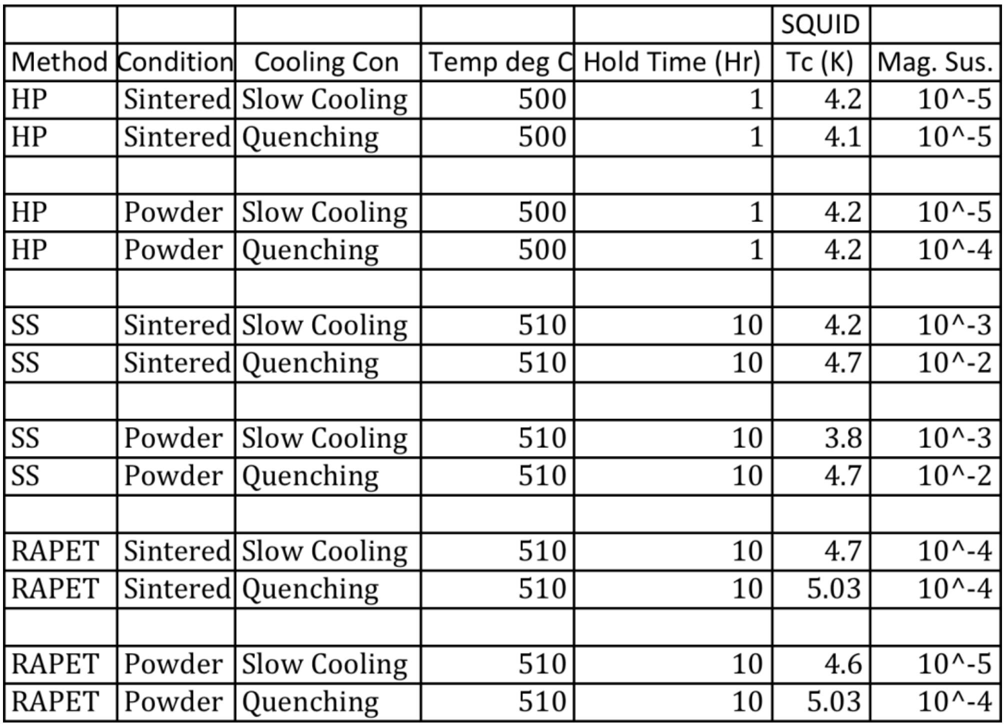
一次燒結的固態燒結法樣品比商用粉末有較高的 Tc，特別是緩慢

的冷卻方法。一次燒結與商業粉末，T_c 有 0.4K 的差別。一次燒結製備的超導比例上升，因此 T_c 和磁化率上升。

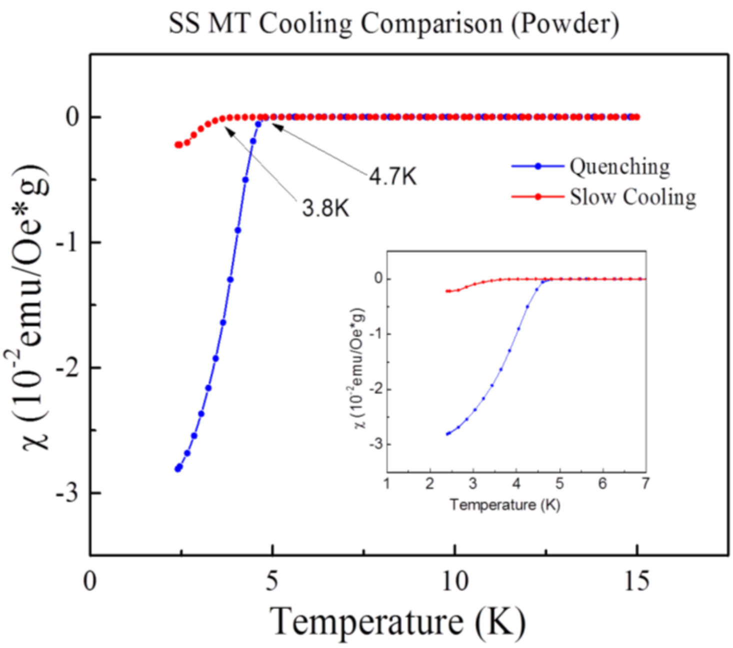
3. RAPET：

通過使用 RAPET 淬火過程樣品性能有相當恒定 T_c 值和磁化率。燒結的樣品有更高 T_c 具有較大的磁化率。

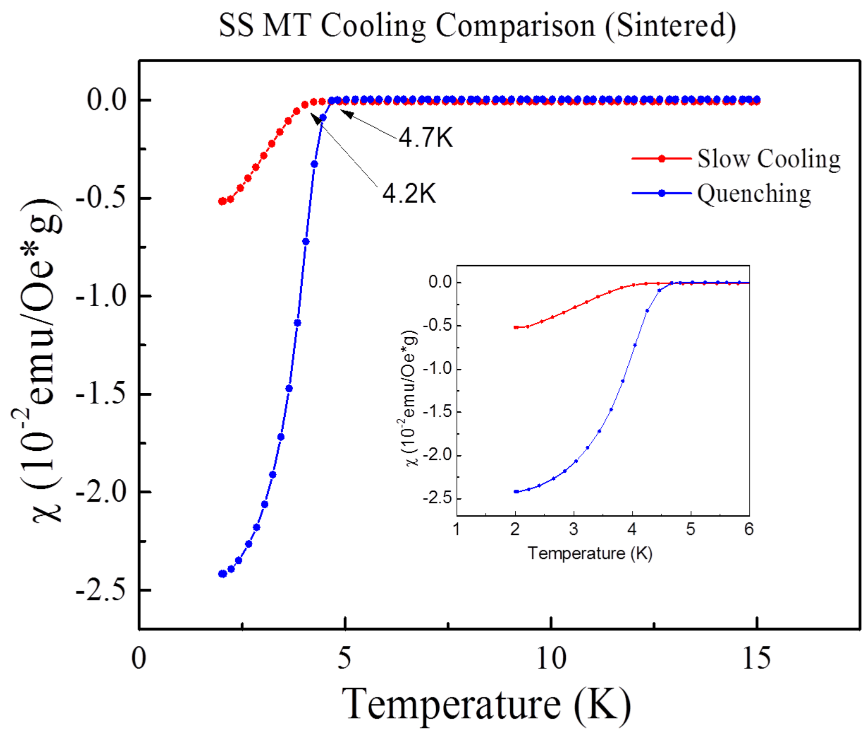
（三)測試冷卻條件



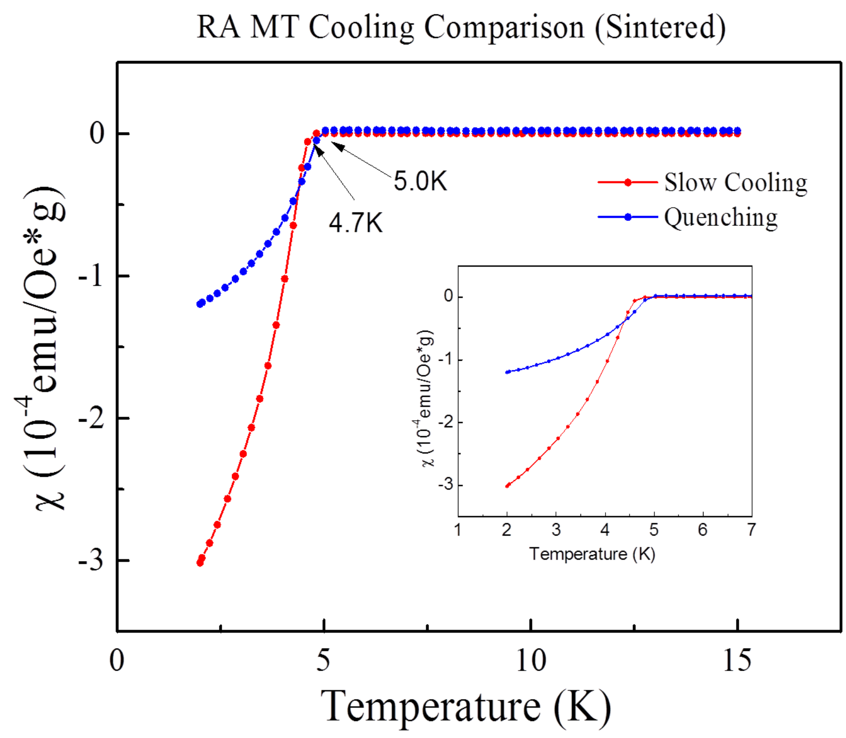
					SQUID	
Method	Condition	Cooling Con	Temp deg C	Hold Time (Hr)	Tc (K)	Mag. Sus.
HP	Sintered	Slow Cooling	500	1	4.2	10^-5
HP	Sintered	Quenching	500	1	4.1	10^-5
HP	Powder	Slow Cooling	500	1	4.2	10^-5
HP	Powder	Quenching	500	1	4.2	10^-4
SS	Sintered	Slow Cooling	510	10	4.2	10^-3
SS	Sintered	Quenching	510	10	4.7	10^-2
SS	Powder	Slow Cooling	510	10	3.8	10^-3
SS	Powder	Quenching	510	10	4.7	10^-2
RAPET	Sintered	Slow Cooling	510	10	4.7	10^-4
RAPET	Sintered	Quenching	510	10	5.03	10^-4
RAPET	Powder	Slow Cooling	510	10	4.6	10^-5
RAPET	Powder	Quenching	510	10	5.03	10^-4

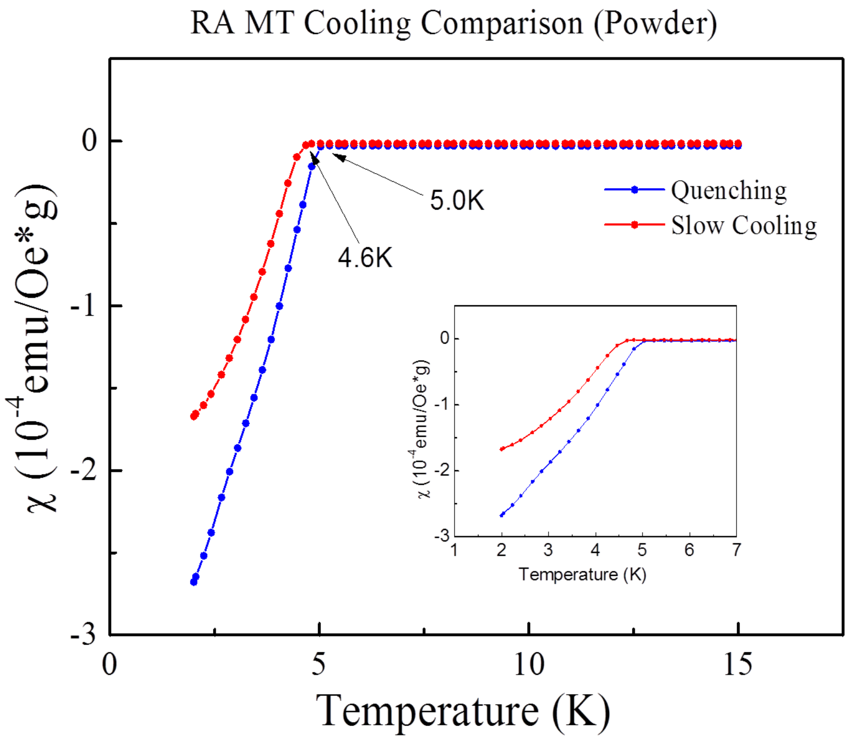


SS MT Cooling Comparison (Powder)



SS MT Cooling Comparison (Sintered)





1. 高壓合成法：

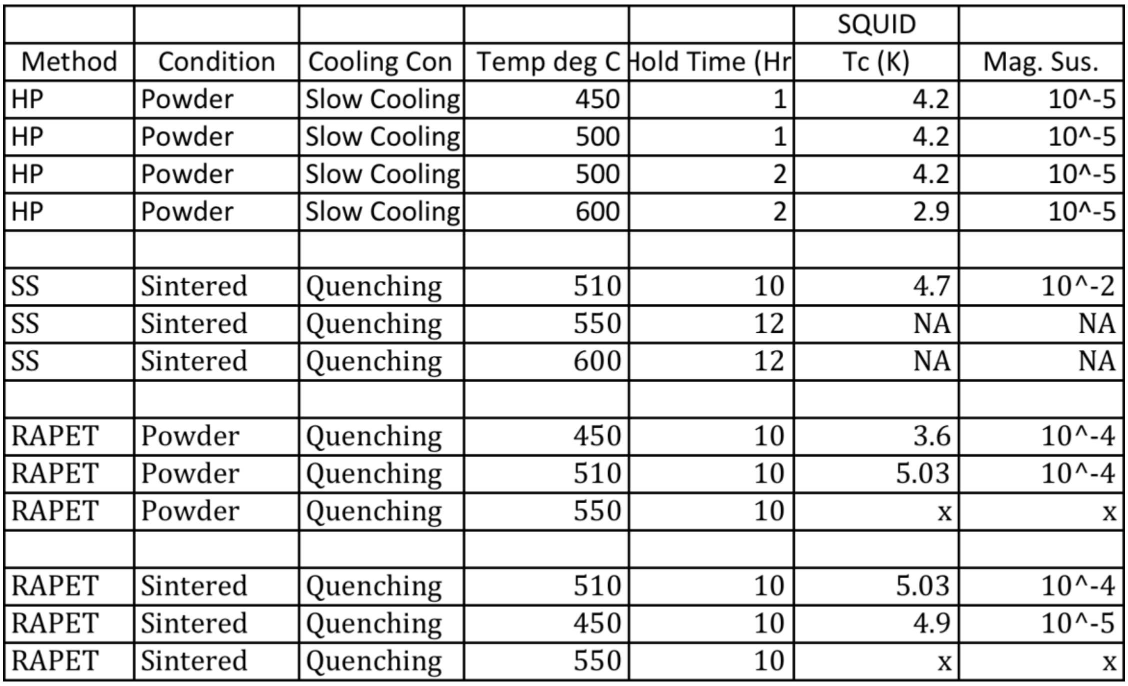
正如之前所說，高壓合成法，緩慢冷卻和淬火具有類似的結果。

2.　固態燒結法：

通過比較固態燒結法，淬火似乎改善 T_c ，和磁化率。T_c 具有增加了幾乎 1 K，而淬火的磁化率是緩慢冷卻的 10 倍左右。這意味著，超導百分比的大幅增加。

3.　RAPET：

淬火的 T_c 高於的緩慢冷卻約 0.4 K。淬火樣本有較大的磁化率。



					SQUID	
Method	Condition	Cooling Con	Temp deg C	Hold Time (Hr	Tc (K)	Mag. Sus.
HP	Powder	Slow Cooling	450	1	4.2	10^-5
HP	Powder	Slow Cooling	500	1	4.2	10^-5
HP	Powder	Slow Cooling	500	2	4.2	10^-5
HP	Powder	Slow Cooling	600	2	2.9	10^-5
SS	Sintered	Quenching	510	10	4.7	10^-2
SS	Sintered	Quenching	550	12	NA	NA
SS	Sintered	Quenching	600	12	NA	NA
RAPET	Powder	Quenching	450	10	3.6	10^-4
RAPET	Powder	Quenching	510	10	5.03	10^-4
RAPET	Powder	Quenching	550	10	x	x
RAPET	Sintered	Quenching	510	10	5.03	10^-4
RAPET	Sintered	Quenching	450	10	4.9	10^-5
RAPET	Sintered	Quenching	550	10	x	x

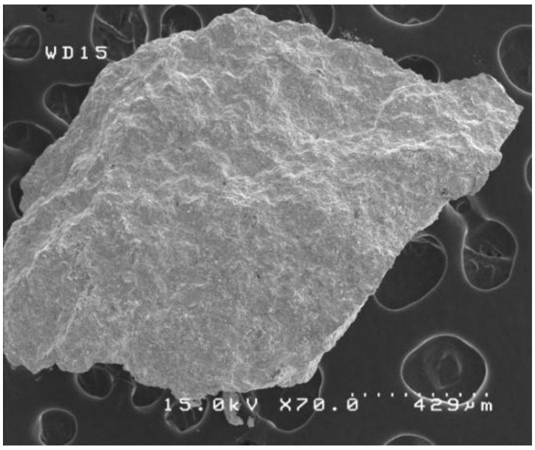
(四)測試溫度條件

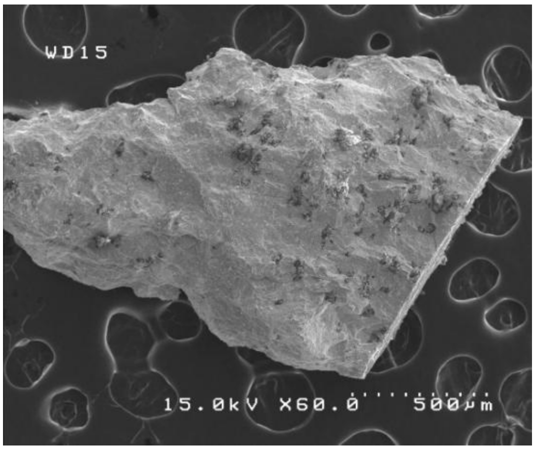
高壓合成法往往於 600 攝氏度仍有超導電性。固態燒結法和 RAPET 低於 550 攝氏度，超導性存在的範圍較小。這可能是由 RAPET 和固態燒結法中硫的缺乏導致的。

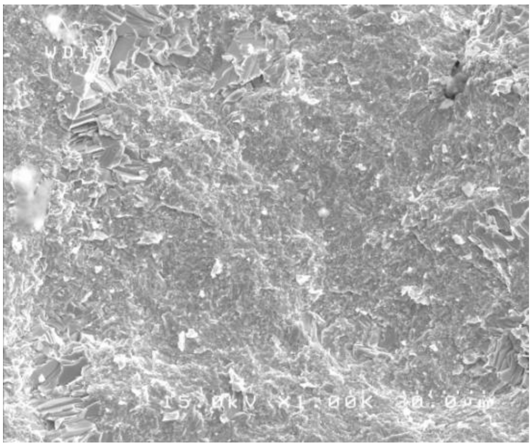
高壓合成法的優點之一是它可防止硫離開，而 RAPET 和固體燒結法並不能。通過 XRD 和 EDX 可以確定是否這一假設可能是真的。

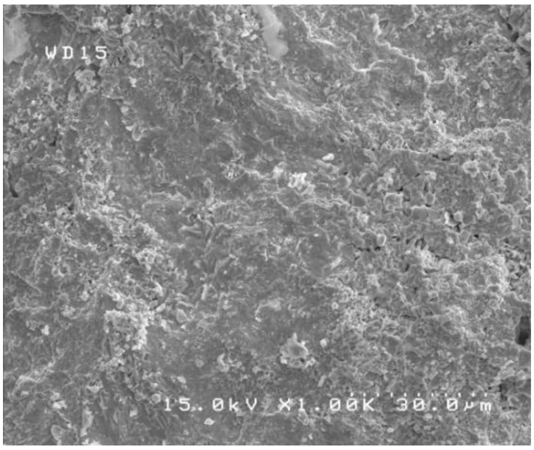
二、化學分析

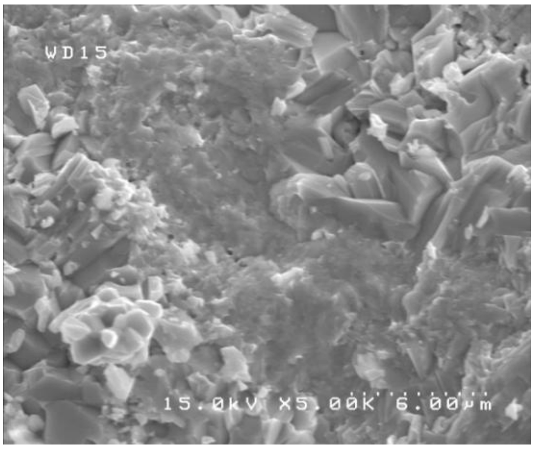
High Pressure Synthesis SEM Pictures and EDX Data

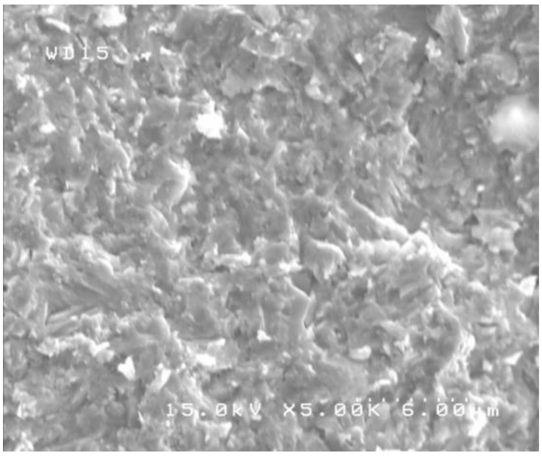


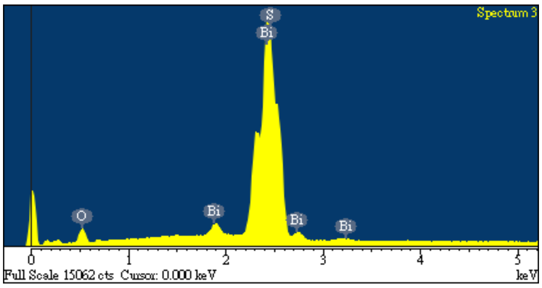


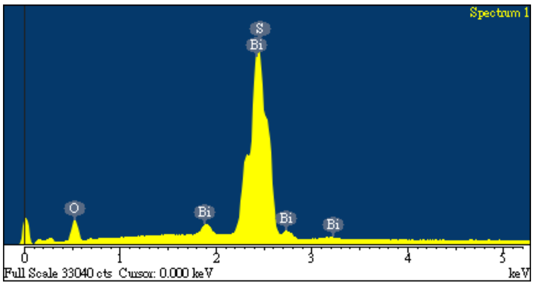






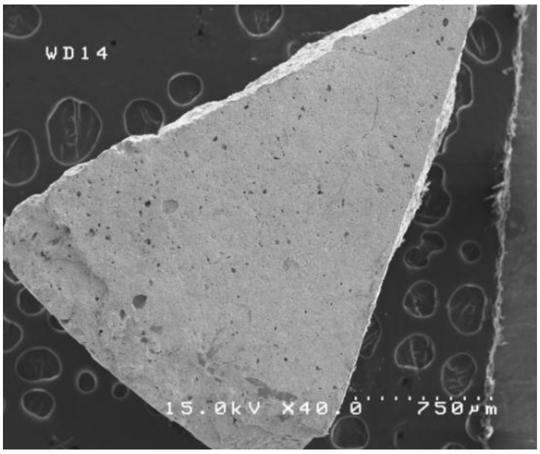


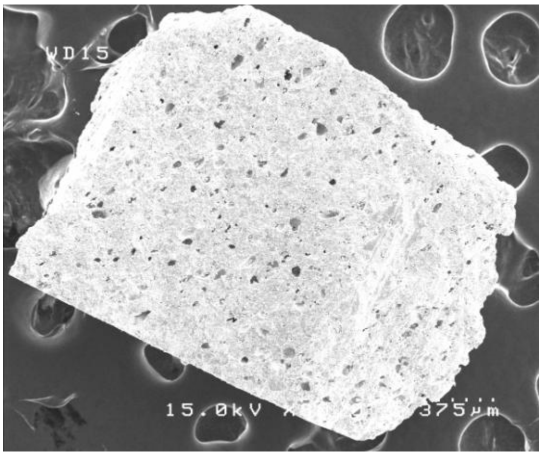


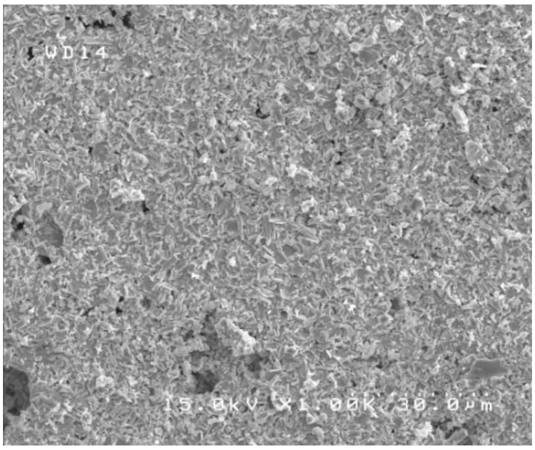


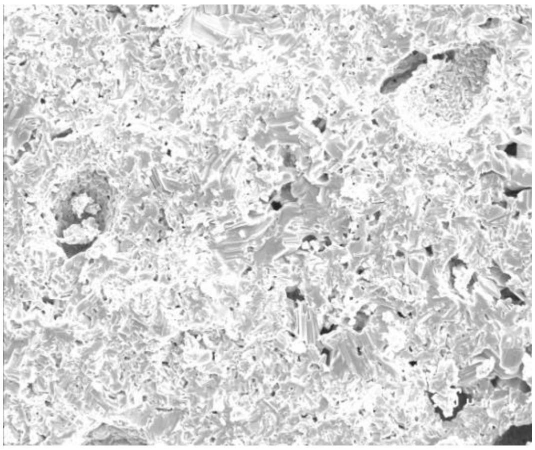
BOS4_1					
element	atomic weight	mass%	mol%	total	real rate
Bi	208.98037	80.62	0.38577786	1.32678527	0.29076134
O	16	10.75	0.671875	1.32678527	0.50639317
S	32.066	8.63	0.26913241	1.32678527	0.20284549
BOS9_1					
element	atomic weight	mass%	mol%	total	real rate
Bi	208.98037	82.91	0.39673583	1.26006517	0.31485342
O	16	10.55	0.659375	1.26006517	0.52328643
S	32.066	6.54	0.20395434	1.26006517	0.16186016

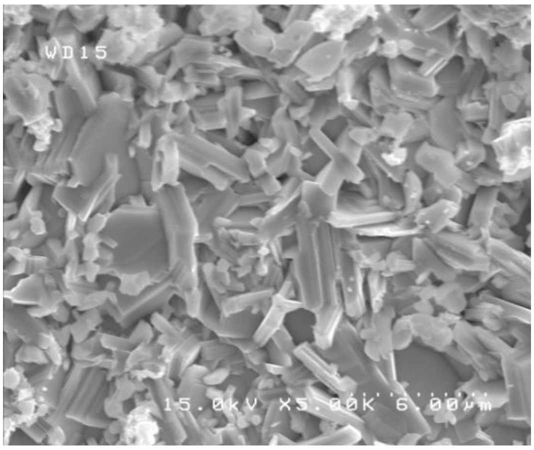
Solid State Reaction Method of SEM Pictures and EDX Data

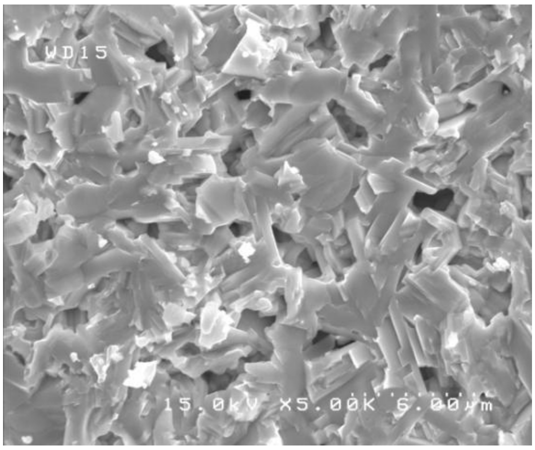


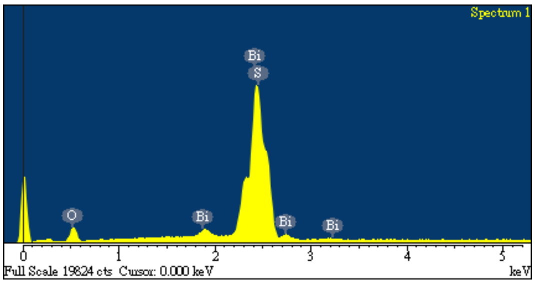


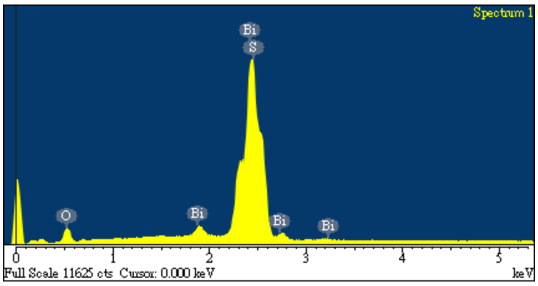






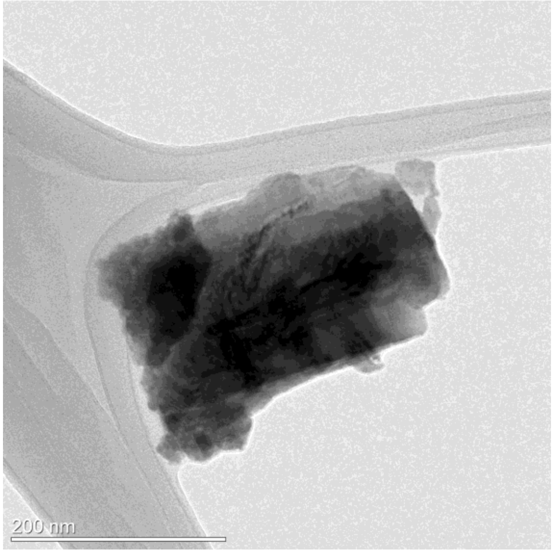


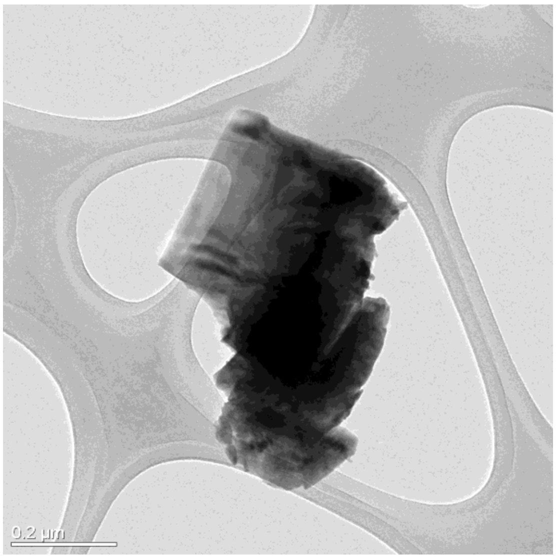


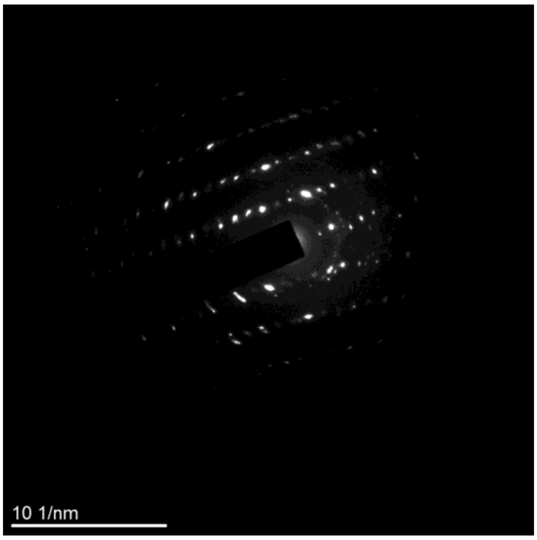


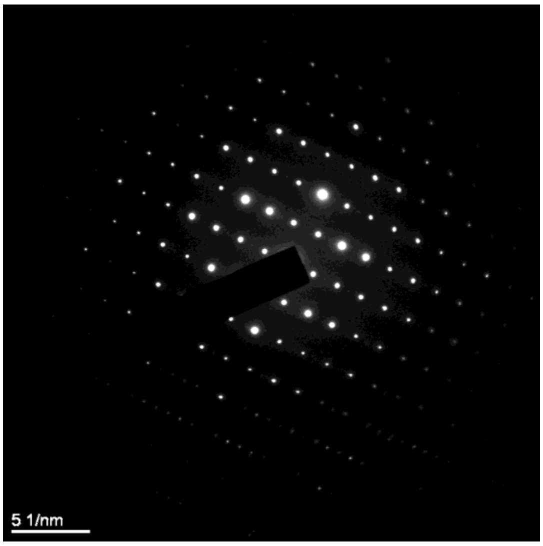
BOS7_1					
element	atomic weight	mass%	mol%	total	real rate
Bi	208.98037	82.38	0.3941997	1.23804599	0.31840473
O	16	9.4	0.5875	1.23804599	0.47453811
S	32.066	8.22	0.25634629	1.23804599	0.20705716
BOS11_1					
element	atomic weight	mass%	mol%	total	real rate
Bi	208.98037	82.57	0.39510888	1.19576713	0.33042293
O	16	8.22	0.51375	1.19576713	0.42964051
S	32.066	9.2	0.28690825	1.19576713	0.23993656

RAPET TEM Pictures and EDX Data

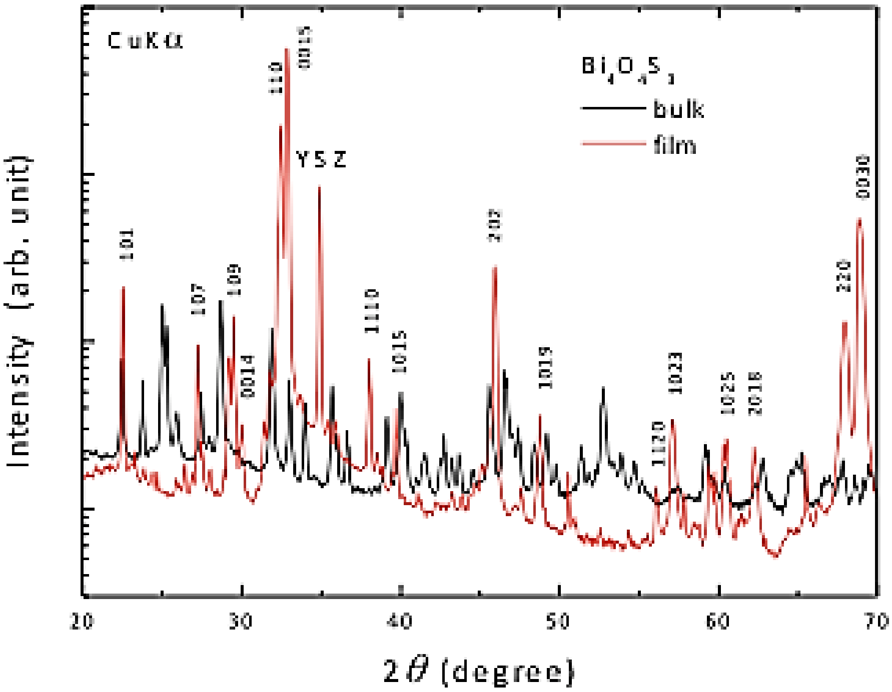


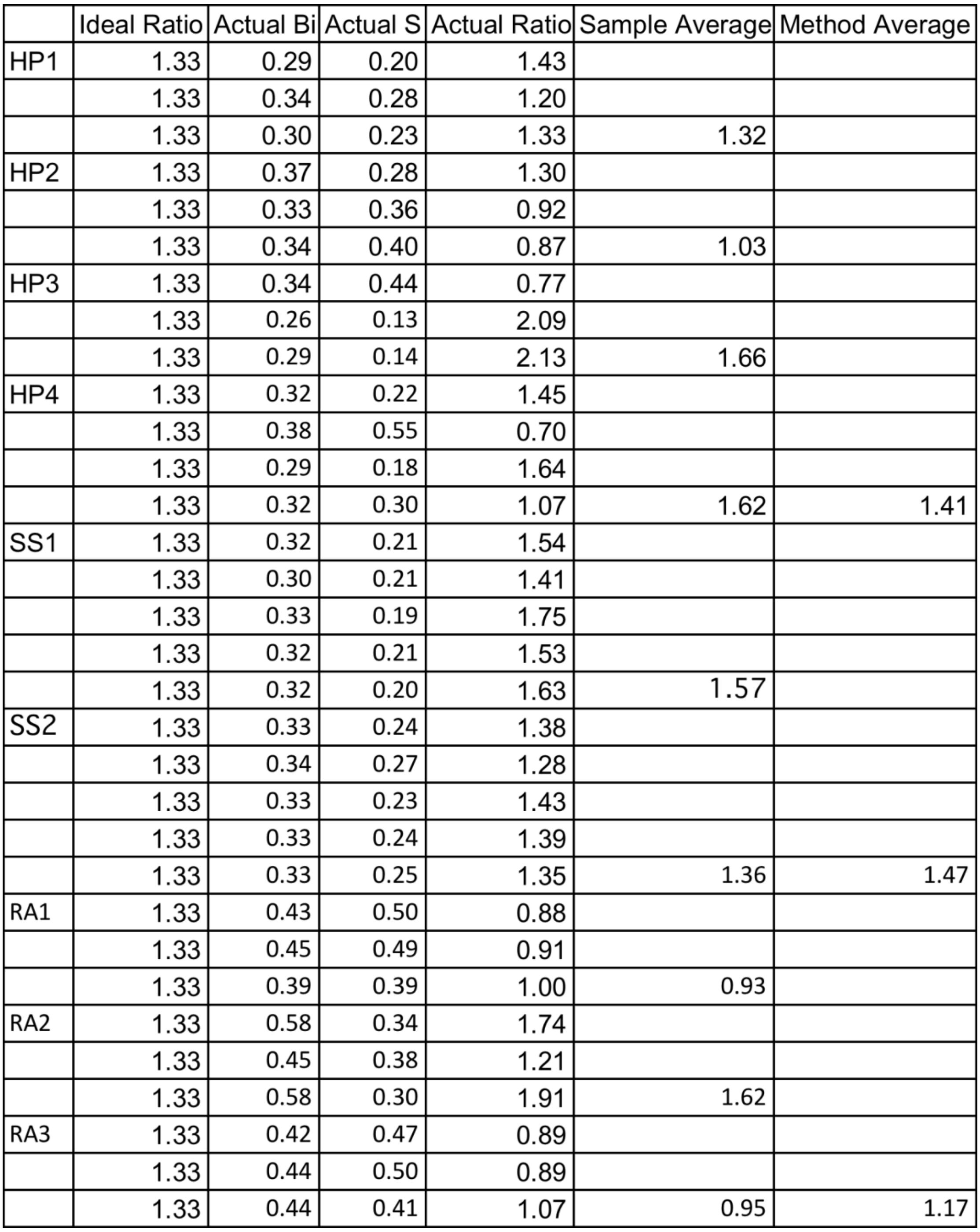






RBOS1_2					
element	atomic weight	mass%	mol%	total	real rate
Bi	208.98037	84.9	0.40625825	0.9031529	0.44982223
O	16	0.83	0.051875	0.9031529	0.05743767
S	32.066	14.27	0.44501965	0.9031529	0.4927401
RBOS2_1					
element	atomic weight	mass%	mol%	total	real rate
Bi	208.98037	91.03	0.43559115	0.74476344	0.58487182
O	16	0.95	0.059375	0.74476344	0.0797233
S	32.066	8.01	0.24979729	0.74476344	0.33540488


CuKα
$Bi_4O_4S_3$
bulk
film
110
0015
YSZ
101
107
109
0014
1110
1015
202
1019
1120
1023
1025
2018
220
0030
Intensity (arb. unit)
20
30
40
50
60
70
2θ (degree)



	Ideal Ratio	Actual Bi	Actual S	Actual Ratio	Sample Average	Method Average
HP1	1.33	0.29	0.20	1.43		
	1.33	0.34	0.28	1.20		
	1.33	0.30	0.23	1.33	1.32	
HP2	1.33	0.37	0.28	1.30		
	1.33	0.33	0.36	0.92		
	1.33	0.34	0.40	0.87	1.03	
HP3	1.33	0.34	0.44	0.77		
	1.33	0.26	0.13	2.09		
	1.33	0.29	0.14	2.13	1.66	
HP4	1.33	0.32	0.22	1.45		
	1.33	0.38	0.55	0.70		
	1.33	0.29	0.18	1.64		
	1.33	0.32	0.30	1.07	1.62	1.41
SS1	1.33	0.32	0.21	1.54		
	1.33	0.30	0.21	1.41		
	1.33	0.33	0.19	1.75		
	1.33	0.32	0.21	1.53		
	1.33	0.32	0.20	1.63	1.57	
SS2	1.33	0.33	0.24	1.38		
	1.33	0.34	0.27	1.28		
	1.33	0.33	0.23	1.43		
	1.33	0.33	0.24	1.39		
	1.33	0.33	0.25	1.35	1.36	1.47
RA1	1.33	0.43	0.50	0.88		
	1.33	0.45	0.49	0.91		
	1.33	0.39	0.39	1.00	0.93	
RA2	1.33	0.58	0.34	1.74		
	1.33	0.45	0.38	1.21		
	1.33	0.58	0.30	1.91	1.62	
RA3	1.33	0.42	0.47	0.89		
	1.33	0.44	0.50	0.89		
	1.33	0.44	0.41	1.07	0.95	1.17

上方的圖片有兩種 SEM 圖，由高壓合成和固態合成法製成。高壓合成樣品表面比固固態合成法樣品來的粗糙。但是，兩個樣品已被均勻合成，圖上只有一些坑洞並沒有許多不同顏色的物質。粗糙樣品的 T_c 似乎比光滑樣品的 T_c 低。

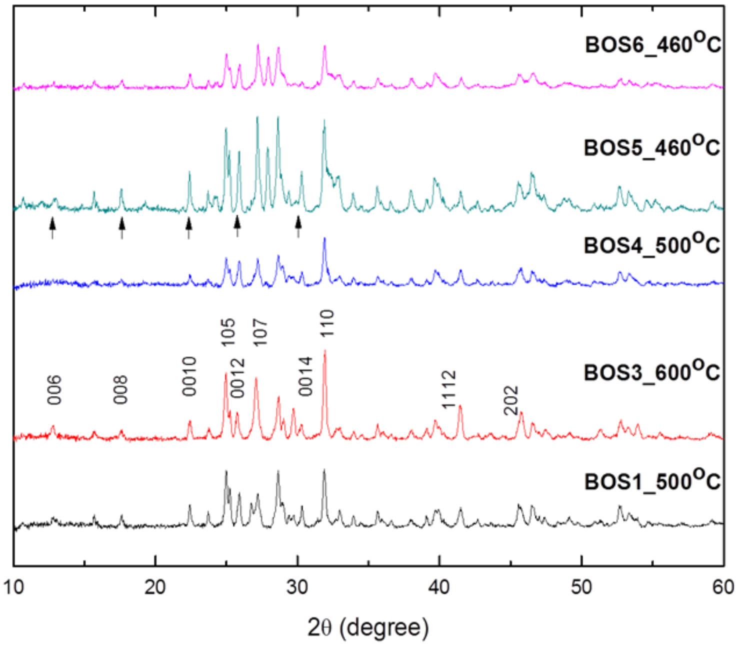
RAPET 在 TEM 圖中大約大小為 100 納米 。這是比上述兩個 SEM

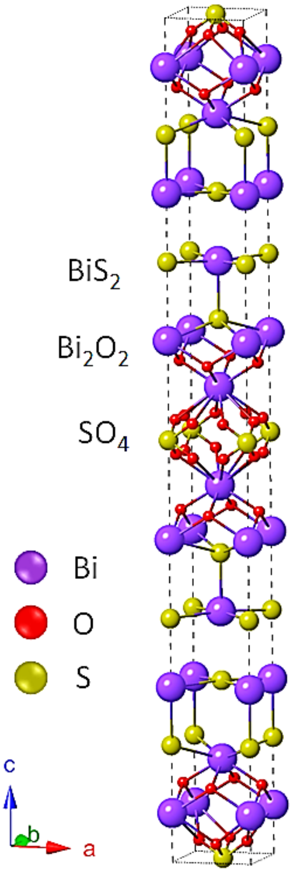
樣品小得多。這兩張照片顯示，該樣品從它的長方狀圖像可以看出它呈層狀結構。因此，RAPET 具有高 Tc 的原因就是因為它的微小尺度。

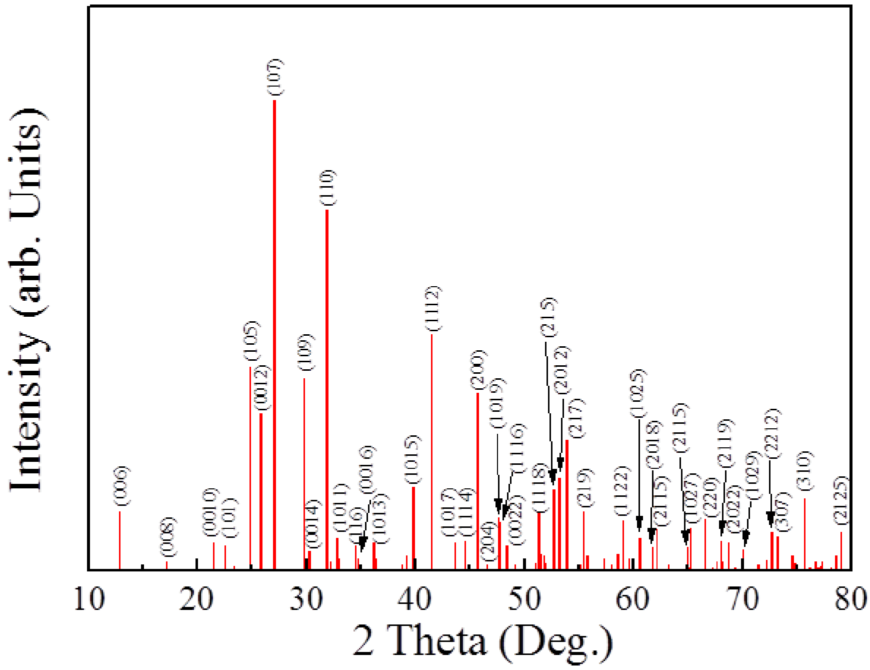
由於樣品的平滑性可能會影響 T_c，那麼另一種增加 T_c 的方式就是讓樣品非常的平滑。通過 PLD，樣品應呈平滑且從多晶變為單晶。XRD 顯示，它的多晶樣品峰的數量越來越少，但並沒有成為一個單晶。嘗試了許多次，由於 $Bi_4O_4S_3$ 結構略複雜，所以無法把它變成一個單晶來看看是否有可能發生 Tc 的改變。

三、結構分析

下面的圖顯示 Bi4OeS3 的分層結構。通過使用 Crystal Maker 的軟體，產生 Bi4OeS3 的原子結構，我們將能夠以可視化的結構，分析可能的摻雜元素。XRD 也可以由該軟體計算產生，並與實際的實驗數據相比。







玖、 結論

通過實驗結果發現了許多不同條件下的樣品有截然不同的結果。RAPET 的方式的臨界溫度最高，比目前其他論文都來的高，可能是因為奈米化及較均勻的結果。在日後的實驗，可以考慮以奈米化當作提升 T_c 的方式。而高壓合成法則是讓 $Bi_4O_4S_3$ 的 4:4:3 比例維持在最佳狀態，對於易揮發物質像硫(S)等可以使用高壓方式來控制材料的比例。固態合成法讓樣品的超導比例最高，達到的 T_c 也相當好。在 500 度經過燒結以及淬火可以達到的超導比例以及臨界溫度都是實驗上得到最高的。通過目前的實驗，條件都可以被控制到相當好，接下來可以從其他條件例如繼續參雜不同元素來提升 T_c.

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評語

1. 作品題材較新穎，探討 Bi-S 系統的超導性，能以 Pb 雜摻嘗試提升相變溫度。
2. X-光譜圖、磁化率及磁矩數據，應可進一步分析，得到較模型化的數據。
3. 奈米化而能提升相變溫度的討論及數據支持應大幅加強。
4. 定量分析的探究應大幅加強。

Abstract

Exotic non-BCS type superconductors are often seen in quasi-two-dimensional materials. Recently, superconductivity with superconducting transition temperature T_C reaches 4.4 K has been reported in a newly synthesized BiS_2-based $Bi_4O_4S_3$ [1,2]. It is known that chemical deficiency can severely affect the superconducting properties. There are several methods that can be used for fabricating ceramic materials.

In this project, I studied the superconducting properties of $Bi_4O_4S_3$ and $LaOBiS_2$ that are synthesized using the three methods and two cooling processes. Each of the high-pressure synthesis, solid-state reaction and reactions under autogenic pressure at elevated temperature (RAPET) method can provide a unique chemical environment for crystallization. Slow cooling in room temperature allows the atoms to crystalize in the designed structure, while rapid quenching in liquid nitrogen can provide severe chemical disorder. Results show that chemical disorder created by RAPET or by rapid quenching plays an effective role in the development of superconductivity in BiS_2-based oxides. A 15% S-deficiency in tri-layered $Bi_4O_4S_3$ created by RAPET with rapid quenching raises the superconducting T_C by 11%. Surprisingly, superconductivity does appear in the bi-layered $LaOBiS_2$ created by RAPET with rapid quenching. A 25% Bi-deficiency was observed in the sample, which triggered the development of superconductivity.

Acknowledgements

I would like to thank Prof. M. K. Wu, for his enthusiasm, his encouragement, and his resolute dedication to my research. I would like to thank Prof. W. H. Li especially for his patience and willingness to help me with the simulations dealt with data analysis of my project. I am also indebted to Dr. W. H. Chao and other senior fellows of Superconductor Laboratory, Institute of Physics, Academia Sinica whose passion for science has inspired me to take my own passions seriously.

I would like to thank National Tsing Hua University for their embracement of diversity, allowing me to take courses in my high school years, where I gained much more knowledge about sciences.

I would like to thank my family—my mom, Annie, and my dad, Jeffrey—for their love, support, and encouraging me to strive for excellence. And finally, though he can't possibly know how much of a help he has been, I'd like to thank Milo (yes, I thanked my dog), who puts the “companion” in “companion animal.”

Table of Contents

I. Introduction

Superconductivity is a phenomenon of zero electrical resistance and exhibits diamagnetism when cooled below a critical temperature. Superconductivity has been discovered in 1910s, when Mercury was found to have zero resistivity in low temperature. After this huge discovery, an issue continued for a couple of decades, there had not been a rise of transition temperature (T_C) as expected. Later on, the discovery of copper oxide based (cuprates) superconductors introduced a new generation of high-T_C cuprates.

The main influence of the high critical temperature of cuprates is its low dimensionality, forming a layer structure. Low dimensionality plays a very important role in condensed mater physics, which favors strong fluctuations of ordering parameters of charge, spin, orbital and lattice in strongly correlated system. Mizuguchi et al. had recently discovered a novel BiS_2-based superconductor, $Bi_4O_4S_3$. It attracted a lot of attention due to its analogies to cuprates and iron-based superconductors. The goal of my project is to find major causes that contribute to the increase of critical temperature of BiS_2-based layered superconductors. After the determination of various factors such as synthesizing temperature and time, I experimented with three different reaction methods along with two cooling processes. Results show that chemical disorder created by RAPET or by rapid quenching plays an effective role in the development of superconductivity in BiS_2-based oxides.

II. Materials and Methods

(I). Apparatus

1. Synthesis

(1) High Pressure Cubic Anvil Synthesis, TRYCA 350 SANKYO

(2) Solid State Reaction Method

(3) RAPET Method (Reactions under Autogenic Pressure at Elevated Temperature)

2. Analysis

(1) XRD (X-ray Diffractometer), PANalytical X’Pert X-ray Diffraction

(2) EDX (Energy Dispersive X-ray)

(3) SEM (Scanning Electron Microscope)

(4) TEM (Transmission Electron Microscope)

(5) SQUID (Superconducting Quantum Interference Device) Quantum Design

(6) PPMS (Physical Property Measurement System), Quantum Design 6000

(II). Experimental Preparation

1. Material Preparation

Figure 1. Chemicals used in this project

Table 1. Chemical names

Chemical Name	Abbreviation	Manufacture
Bismuth Powder	Bi	Alfa Aesar
Bismuth Oxide	Bi_2O_3	Cerac
Sulfur	S	Riedel-deHaen
Bismuth(III) Sulfide	Bi_2S_3	Sintering Bismuth and Sulfur powder
Bismuth(III) Telluride	Bi_2Te_3	Alfa Aesar
Bismuth(III) Selenide	Bi_2Se_3	Alfa Aesar

Chemical formulas

$Bi_4O_4S_3$ Commercial Powder:

$4Bi_2O_3+4Bi+9S \rightarrow 3\ Bi_4O_4S_3$

$Bi_4O_4S_3$ First Sinter:

$Bi_2S_3+4Bi_2O_3+3S \rightarrow 3\ Bi_4O_4S_3$

$Bi_4Te_4S_3$ Powder:

$4Bi_2Te_3+4Bi+9S \rightarrow 3Bi_4Te_4S_3$

$Bi_4Se_4S_3$ Powder:

$4Bi_2Se_3+4Bi+9S \rightarrow 3Bi_4Se_4S_3$

2. Experimental Preparation

- Convert molecular weight and calculate the appropriate weight of each chemical.
- Grind chemicals together into well-mixed powder.
- Decide synthesizing method and other conditions for commercial powder preparation after grinding while keep preparing for first sintered Bi_2S_3 powder.

- Compress the well-mixed powder into an ingot and prepare by solid state reaction method with the condition of 510 degrees for 10 hours to prepare for sintered Bi_2S_3 powder.

3. Cooling Process

(1) Slow Cooling

- Wait until the sample cool off to room temperature.

(2) Quenching

- Prepare liquid nitrogen, beaker, and a clamp.
- Put sample into the beaker and pick the beaker up by a clamp, and put the beaker half way into the liquid nitrogen to let sample cool down fast enough.
- We use liquid nitrogen for cooling for two main reasons. If cool our samples by water and the water spills into the sample, it might contaminate the sample while liquid nitrogen turns into gas. Another reason is that liquid nitrogen is much colder than water, which drops the sample temperature faster than water.

(III). Reaction Methods

1. Solid State Reaction Method

Figure 2. Tube heater

(1) Brief Description of Solid State Reaction Method

The solid state reaction method could be used to prepare a large range of materials from metal oxides, sulfides and more. This method could be used to prepare a large number of compounds. The only required machineries are sealing and heating machines, which would be easier to have rather than RAPET or high pressure synthesis. In comparison to other methods like high pressure synthesis, the created sample would be much larger in amount. Although, solid state reaction method takes a longer time throughout the sample making process, but it may be more effective after determining the favorable temperature, time, and sample condition.

(2) Apparatuses and Materials

- Quartz Tube
- Tube Sealer
- Tube Heater

(3) Procedure

- High purity chemicals of $Bi_4O_4S_3$ are weighed in the correct stoichiometric ratio to about 2g to create the ingot.
- Grind and mix the appropriate chemicals that makes the $Bi_4O_4S_3$ compound.
- Compress compounds into ingot with the weight of 3 tons for 15 minutes.
- Evacuate Quartz tube with the tube sealer to 10^{-6} Torr and seal the Quartz tube first by the mechanical pump, then the turbopump.
- Insert quartz tube into the tube heater and program heating condition of the tube heater manually.

2. High Pressure Synthesis Technique

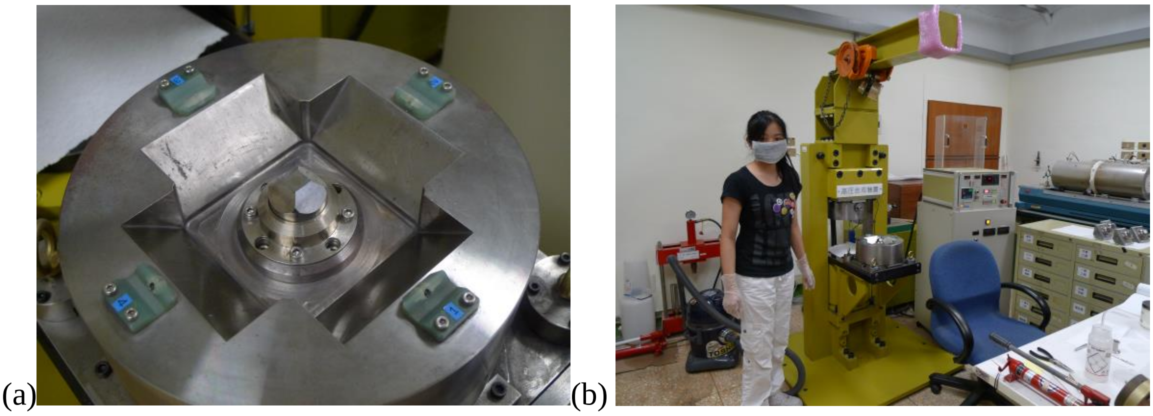

(a) (b)

Figure 3. (a) Interior photo of HPS (b) HPS

(1) Brief Description of High Pressure Synthesis

High pressure synthesis method is more advantageous than other methods while exploring new materials. One can shorten the periods required for the sample synthesis process, which may be extremely useful to find out the condition suitable for the material. The material increases its density through compressing the compound, which may increase the stability by forming new compounds with smaller volume. High pressure synthesis method could also prevent evaporation of toxic elements like As, K, and more.

Throughout the history of cuprate superconductors, high pressure synthesis method has been a powerful tool of the discovery of high T_c superconductors and multi-layer superconductors. Therefore, high pressure synthesis would be a fine choice for new material hunting and determining the time, temperature, and pressure conditions for a new material.

(2) Apparatuses and Materials

- High Pressure Cubic Anvil Synthesis, TRYCA 350 SANKYO
- Boron Nitride powder (to make Boron Nitride tubes and disks)
- Graphite tubes and plates
- Stainless steel Rings
- Pyrophyllite plates and cubes ($Al_2Si_4O_{10}(OH)_2$)
- Molybdenum plates

(3) Procedures

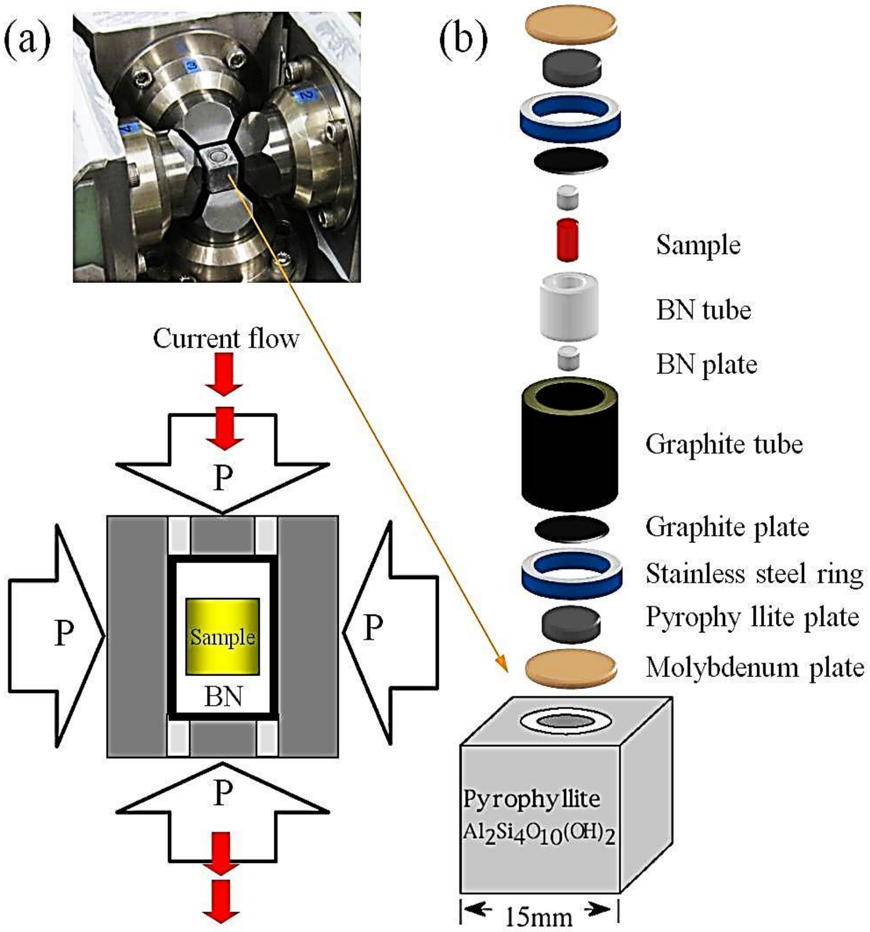


Figure 4. (a) (b) High Pressure Routine

- High purity chemicals of $Bi_4O_4S_3$ are weighed in the correct stoichiometric ratio.
- Grind and mix the appropriate chemicals that makes the $Bi_4O_4S_3$ compound
- Compress 0.36g of $Bi_4O_4S_3$ into an appropriate size pellet and encapsulated into closed container made of Boron Nitride tube and plates.

- Place the sample with Boron Nitride into graphite tube and disks and stack other apparatuses (stainless steel ring, Pyrophyllite plates, and Molybdenum plates) in an order of the picture shown below.
- Assemble the stack into the Pyrophyllite cube and insert it into wedge-type cubic anvil.
- Insert the whole cubic anvil into the high pressure apparatus.
- Adjust the high pressure apparatus and program the temperature and current conditions of the sample manually with drawn out condition as the picture below.
- Press the button that activates the pressure pump to increase the sample up into the high pressure apparatus, then run the pressure program.
- Manually make slight adjustments of starting pressure (8ml/min), when target pressure is three times the actual, then press to increase to start pressuring the sample.
- Make slight pressure adjustments for the first few minutes because of the elastic and plastic deformation of cubic anvil, then and run the current program.
- Sample starts synthesizing by the high pressure apparatus, and the whole process would be finished as the entered time condition.

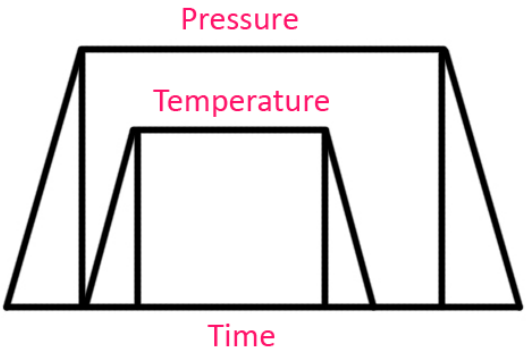


Figure 5. Time and Pressure condition figure

3. RAPET Method (Reactions under Autogenic Pressure at Elevated Temperature)

Figure 6. RAPET Reactor

(1) Brief Description of RAPET Method

RAPET method is a special method that could use to fabricate Nano scale samples. Unlike high pressure synthesis or solid state reaction method, the resulting sample may be quite powdery which may result the difficulty to do analysis such as PPMS (Physical Property Measurement System). Although it may be powdery, but it is a rapid and convenient method, it could also be used as a method that determines sample condition. This is a rare method to use for fabricating samples and the advantages it have makes RAPET a great method for my purpose.

(2) Apparatuses and Materials

- RAPET tube heater
- Switch Lock

(3) Procedure

- High purity chemicals of $Bi_4O_4S_3$ are weighed in the correct stoichiometric ratio to about 2g.
- Grind and mix the appropriate chemicals that makes the $Bi_4O_4S_3$ compound.

- Insert chemicals into the switch lock, and lock the switch lock tightly on both sides to prevent spilling.
- Insert the switch lock into the tube of the tube heater, close all knobs of tube heater.
- Open up a knob by a knob so that each section of tubes are vacuumed section by section with the mechanical pump to about 10^{-4} Torr.
- Once the gauge reaches a point where the tube is fully vacuumed, open up the Argon gas.
- Open up the gas flow button and adjust the amount of gas flow accordingly when it approaches to full.
- Open up a knob of the end of RAPET tube heater for the circulation of Argon gas.
- Program condition manually.

4. PLD (Pulsed Laser Deposition)

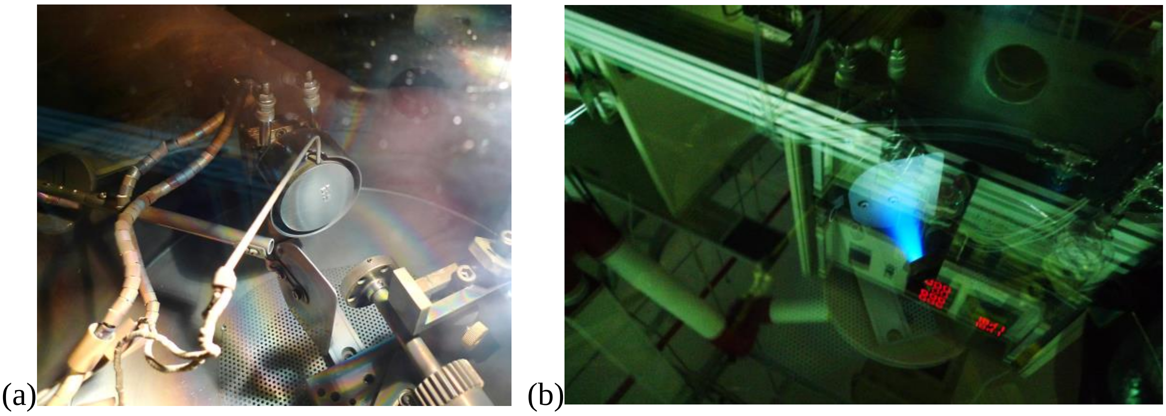

(a) (b)

Figure 7. (a) (b) PLD

(1) Brief Description of PLD

PLD is where a high power pulsed laser beam is focused into a single point inside of a vacuum chamber to strike a target of a material. This material will be vaporized from the target and deposits it as a thin film on a silicon wafer substrate.

(2) Apparatuses and Materials

- Entire set of PLD Apparatus

(3) Procedure

- Set laser program and prepare apparatus setup for PLD
- Adjust focus lens to focus laser correctly
- Insert target
- Turn on laser to start PLD

(IV). Analytical Methods

1. SQUID (Superconducting Quantum Interference Device)

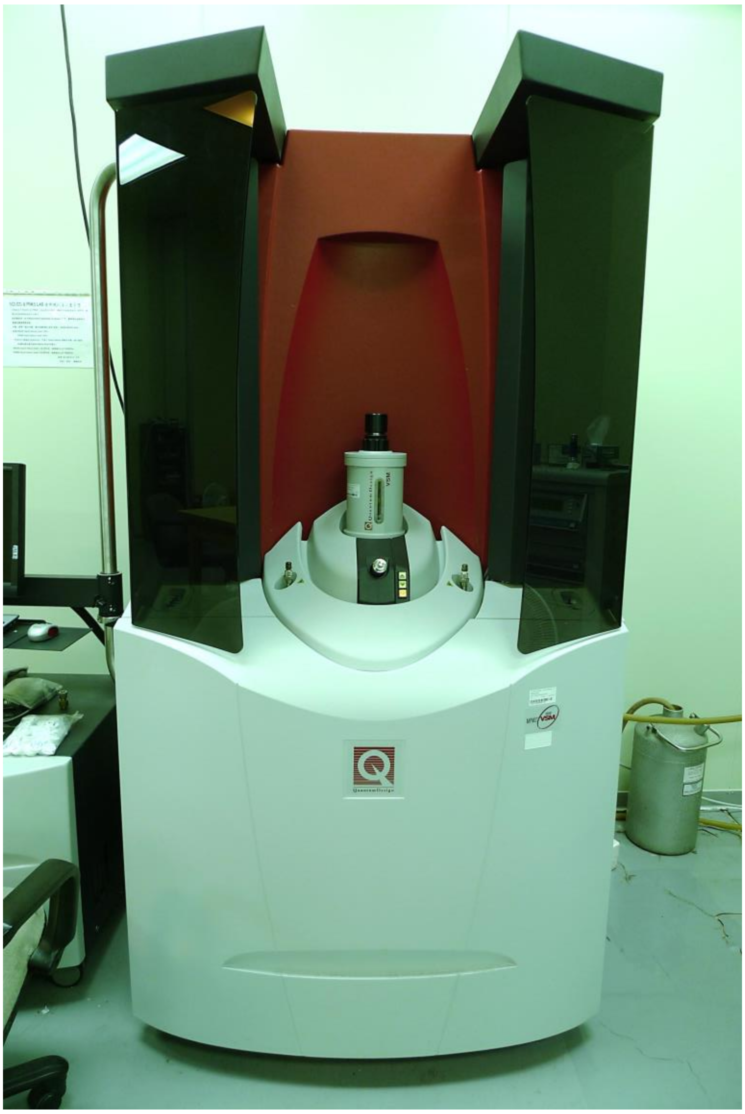


Figure 8. SQUID

(1) Brief Description of SQUID

SQUID, the superconducting quantum interference device is built during 1960s. The SQUIDs are superconducting devices that measure magnetic flux and output voltage signal. The data shows the zero field cooling (ZFC) and field cooling (FC) curves, which indicates its magnetic moment in a specific temperature. To find desire value of magnetic susceptibility, we use the equation of emu/(Oe*g) to determine it. SQUID helps us to find the T_c and the magnetic susceptibility, which makes it an extremely strong method for the analysis of superconductors.

(2) Functions

- Insert sample by small amount of powder contained in a plastic capsule inserted in a plastic straw or by a little piece clipped in a brass straw.
- Screw the brass straw or plastic straw onto the carbon tube and insert it into SQUID when the condition shows 300K for temperature, 0Oe for magnetic field, and Sequence Idle.
- Press button twice to purge and seal for a total of 9 times including the first press that SQUID does automatically once the sample is inserted.
- Locate sample and center it to verify the detecting point.
- Start zero field cooling (ZFC) at the temperature from 300K down to 10K at the rate of 15K/min, and 10K to 2K at the rate of 3K/min.
- After reaching 2K, add field of 10Oe and measure 4 sec/point up to 15K, and this is the ZFC portion of measurement.
- Start field cooling (FC) at 15K and measure back to 2K with 10Oe at the same rate. SQUID measurement is done after raising temperature back to 300K, no field, and shows sequence idle.

2. XRD (X-ray Diffractometer)

Figure 9. XRD Device

(1) Brief Description of XRD

The basics of X-ray Diffraction came from Bragg's Law $n\lambda = 2d\sin\theta$, where he developed the relationship to explain how different faces of crystals appear to reflect X-ray beams at certain angles. It provides the data of the intensity of the beam at different angles. The different peaks represent a certain identity of the material and we would be able to find the contributions of different compounds. Another application of the data would be identifying Miller indices of the crystal faces by the combination of other measurements.

(2) Functions

- Grind sample into powder and place it on the zero diffraction plate that is made of silicon cut at special orientation.
- Flatten the powder sample on the zero diffraction plate and insert it into the XRD.
- Set angle from 10 degrees to 80 degrees ($2q$) to prevent the rays from hitting the detector to create damage of the XRD.

3. PPMS (Physical Property Measurement System)

(1) Brief Description of PPMS

The physical property measurement system generates a data that indicates the resistance of the sample through different temperature. To have a more accurate description, we would have to change the resistance data into resistivity. The resistivity is calculated by the (resistance x width x thickness)/length between the two middle threads. This could more accurately determine the superconductivity of a sample since resistance changes with the size of the sample while the resistivity does not.

(2) Functions

- Prepare hard samples and attach it with four Platinum threads with silver colloid.
- Insert it into the PPMS machine

4. EDX (Energy-dispersive X-ray spectroscopy)

EDX is an analytical technique used for the chemical characterization of a sample. In this case, when we have the EDX data it shows the mass percentage of Bi, O, and S. EDX uses the interaction of some source of X-ray excitation to examine a sample. It emits a beam of charged particles such as electrons to the sample being studied. Therefore we are able to tell what exactly is in the sample and its percentage to examine whether the ratio of the compound remains or fluctuates.

5. SEM (Scanning Electron Microscope)

SEM is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The produced images are usually measured in the unit of micrometer.

Figure 10. SEM

6. TEM (Transmission Electron Microscopy)

TEM is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen producing an image at the unit of nanometers.

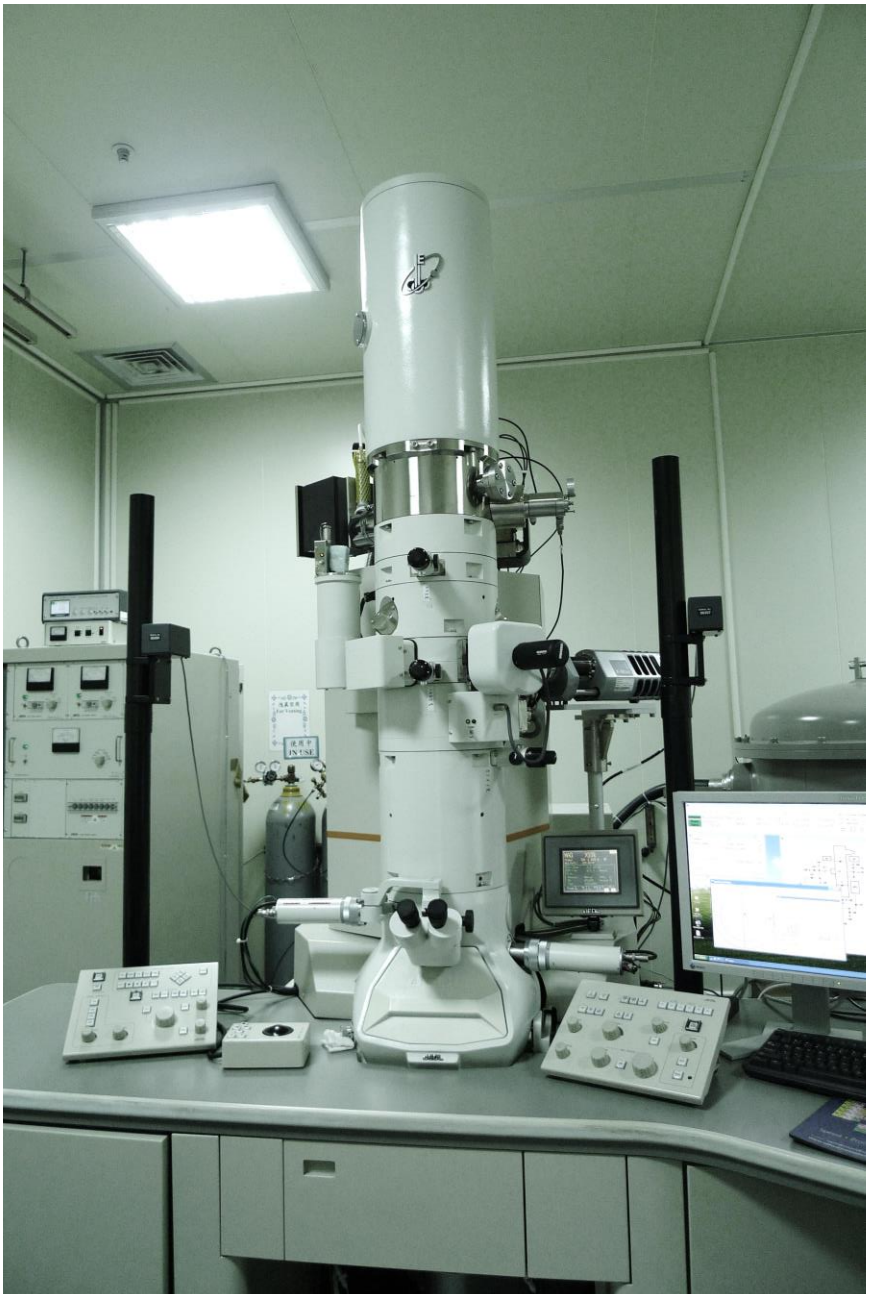


Figure 11. TEM

III. Results

(I). Sample Condition Analysis

1. Testing Temperature Condition

I've chosen high pressure synthesis method as a starting method for this experiment considering its effectiveness for hunting new materials and determining its condition. Setting the starting temperature around 500 degrees by paper surveying for temperature condition of solid state reaction method since there wasn't any paper about high pressure synthesis on $Bi_4O_4S_3$ back then. I've tested three different temperature conditions ranging from 450 to 600 degrees to check whether 500 degrees would be an appropriate synthesizing temperature and analyzing by SQUID and PPMS.

Table 2. Synthesizing temperature data

						SQUID		PPMS
Name	Method	Condition	Cooling Con	Temp deg C	Hold Time (Hr)	Tc (K)	Mag. Sus.	Resistiv (mohm-cm)
HBOS1	HP	Powder	Slow Cooling	600	2	2.9	10^-5	1.05
HBOS2	HP	Powder	Slow Cooling	500	1	4.2	10^-5	2.97
HBOS3	HP	Powder	Slow Cooling	450	1	4.2	10^-5	85.1

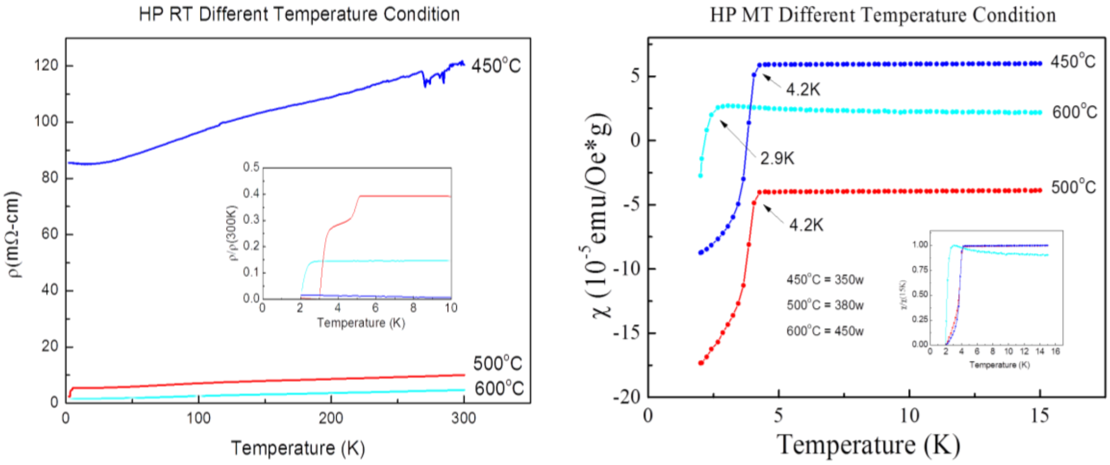


Figure 12. (a) Resistivity to temperature graph (b) Magnetic susceptibility to temperature graph

Through the chart above, we could easily conclude that the T_c is mostly 4.2 while magnetic susceptibility are all consistently 10^{-5}. The only change that we could find is from PPMS, the lowest resistivity is 1.05, but its T_c is much lower than others.

Therefore, we may be able to conclude that the highest Tc with the second lowest resistivity would be our best choice and that is the sample with temperature 500 degrees Celsius.

Besides form the chart, the two graphs show the magnetic susceptibility and resistivity. The graph on the left, data by SQUID shows that 450 and 500 degrees data have better superconductive percentage than the 600 degree one. The graph of the on the right shows that the 500 degree sample has the steepest drop of resistivity, closer to zero resistivity, and have the highest T_c from the PPMS data.

I could conclude that temperature conditions of future samples would be about 500 degrees Celsius. By following the temperature condition, we continued our experiment by comparing different chemical compounding condition and cooling condition.

2. Testing Chemical Compounding Condition

There are two ways to prepare for $Bi_4O_4S_3$, a way with first sintered Bi_2S_3, and a way with just commercial powder. By paper surveying, I've find that couple of papers have proven that the first sintered chemical compound of Bi_2S_3 increases Bismuth Oxysulfide's superconductivity through the solid state method. Therefore, decided to compare the two ways to prepare $Bi_4O_4S_3$ with three synthesizing methods, high pressure synthesis, solid state reaction method, and RAPET. Before experimenting, I had an expectation that first sintered $Bi_4O_4S_3$ would have a higher T_c, greater magnetic susceptibility, and less resistivity.

I prepare first sintered Bi_2S_3 by Bismuth powder and Sulfur powder in by their appropriate ratio and use the solid state reaction method by holding 10 hours at 510 degrees Celsius.

Chemical formulas to prepare $Bi_4O_4S_3$:

Commercial Powder:

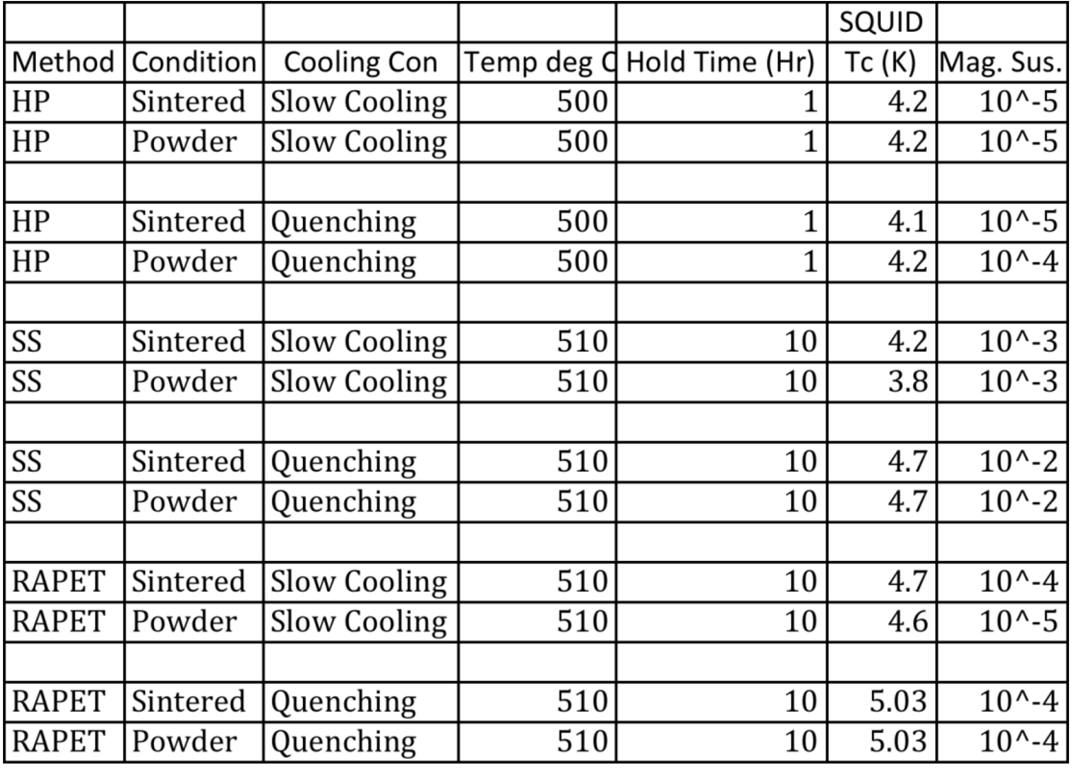
$4Bi_2O_3+4Bi+9S \rightarrow 3\ Bi_4O_4S_3$

First Sintered Bi_2S_3:

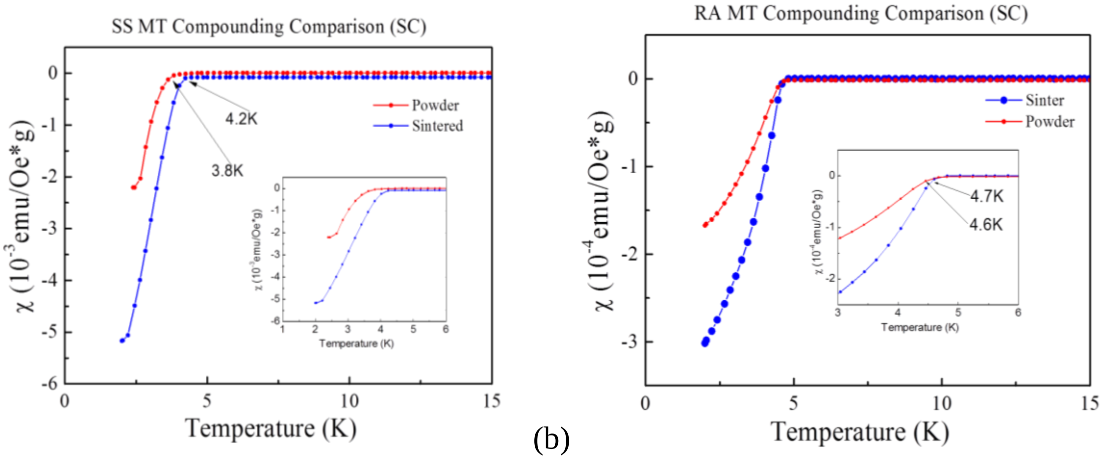
$Bi_2S_3+4Bi_2O_3+3S \rightarrow 3\ Bi_4O_4S_3$

The three different method comparisons are shown on the chart below.

Table 3. Sintered and Powder Sample Table



					SQUID	
Method	Condition	Cooling Con	Temp deg C	Hold Time (Hr)	Tc (K)	Mag. Sus.
HP	Sintered	Slow Cooling	500	1	4.2	10^-5
HP	Powder	Slow Cooling	500	1	4.2	10^-5
HP	Sintered	Quenching	500	1	4.1	10^-5
HP	Powder	Quenching	500	1	4.2	10^-4
SS	Sintered	Slow Cooling	510	10	4.2	10^-3
SS	Powder	Slow Cooling	510	10	3.8	10^-3
SS	Sintered	Quenching	510	10	4.7	10^-2
SS	Powder	Quenching	510	10	4.7	10^-2
RAPET	Sintered	Slow Cooling	510	10	4.7	10^-4
RAPET	Powder	Slow Cooling	510	10	4.6	10^-5
RAPET	Sintered	Quenching	510	10	5.03	10^-4
RAPET	Powder	Quenching	510	10	5.03	10^-4



(a) (b)

Figure 13. (a) Magnetic susceptibility graph of SS (b) Magnetic susceptibility graph of RA

High Pressure Synthesis:

High pressure synthesis sample tend to have similar T_c, despite the difference of compounding condition (sinter or powder). High pressure synthesis of sample shows that the T_c would probably be about 4.2K while magnetic susceptibility would be at about 10^{-4}. Although we are able to generalize its T_c and magnetic susceptibility, but we are unable to determine a pattern from the data. We are unable to determine which compounding condition would have the best superconductivity because of the little changes in the data as well as the inconsistency. The reason of the inconsistency could be further discussed in chemical analysis by EDX.

Solid State Reaction Method:

Solid state sample with first sinter has slightly higher T_c than commercial powder especially with slow cooling method. There's a 0.4K T_c difference between sintered sample and commercial powder sample. This is considerably high for a new material with a low T_c to start with. The length of the drop after T_c on the SQUID MT data has a significant difference. This meant that the superconductive percentage of sintered sample rose. Therefore, both T_c and magnetic susceptibility rose for sintered sample.

RAPET:

The performance of sinter and powder samples during quenching by using RAPET method has rather constant T_c values and magnetic susceptibility. But there's a slight change of T_c and magnetic susceptibility in the slow cooling sinter and powder sample data. The sintered sample has higher T_c with a larger magnetic susceptibility.

Conclusion of Compound Condition:

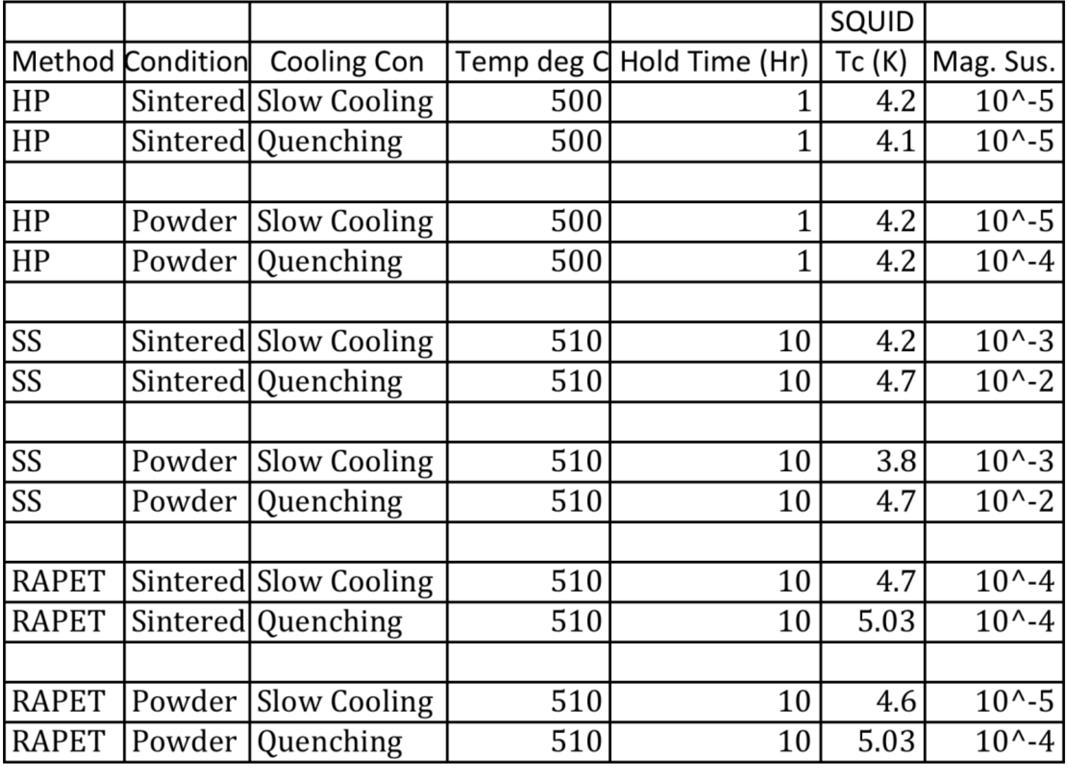
RAPET and solid state reaction method both shows that first sintered BOS has a bit better performance than the powder ones. But high pressure synthesis does not prove that first sintered BOS has better performance than powder ones. Possible reasons of why high pressure synthesis would be less effective in comparison with solid state reaction method is shown below.

- *EDX shows that high pressure synthesis by our condition does not provide uniform BOS.*
- *Why did quenching samples of different compounding condition remain the same T_c while the slow cooling samples change? Possible structural change through quenching?*
- *Possibly needs to increase the time at its highest temperature considering that both RAPET and solid state reaction method, we used about 10 hours while we only have 1 hour during high pressure synthesis*

3. Testing Cooling Condition

Another condition factor that we could change to increase its T_c, magnetic susceptibility, or resistivity is by changing its cooling temperature through slow cooling or quenching.

Table 4. Cooling condition results



					SQUID	
Method	Condition	Cooling Con	Temp deg C	Hold Time (Hr)	Tc (K)	Mag. Sus.
HP	Sintered	Slow Cooling	500	1	4.2	10^-5
HP	Sintered	Quenching	500	1	4.1	10^-5
HP	Powder	Slow Cooling	500	1	4.2	10^-5
HP	Powder	Quenching	500	1	4.2	10^-4
SS	Sintered	Slow Cooling	510	10	4.2	10^-3
SS	Sintered	Quenching	510	10	4.7	10^-2
SS	Powder	Slow Cooling	510	10	3.8	10^-3
SS	Powder	Quenching	510	10	4.7	10^-2
RAPET	Sintered	Slow Cooling	510	10	4.7	10^-4
RAPET	Sintered	Quenching	510	10	5.03	10^-4
RAPET	Powder	Slow Cooling	510	10	4.6	10^-5
RAPET	Powder	Quenching	510	10	5.03	10^-4

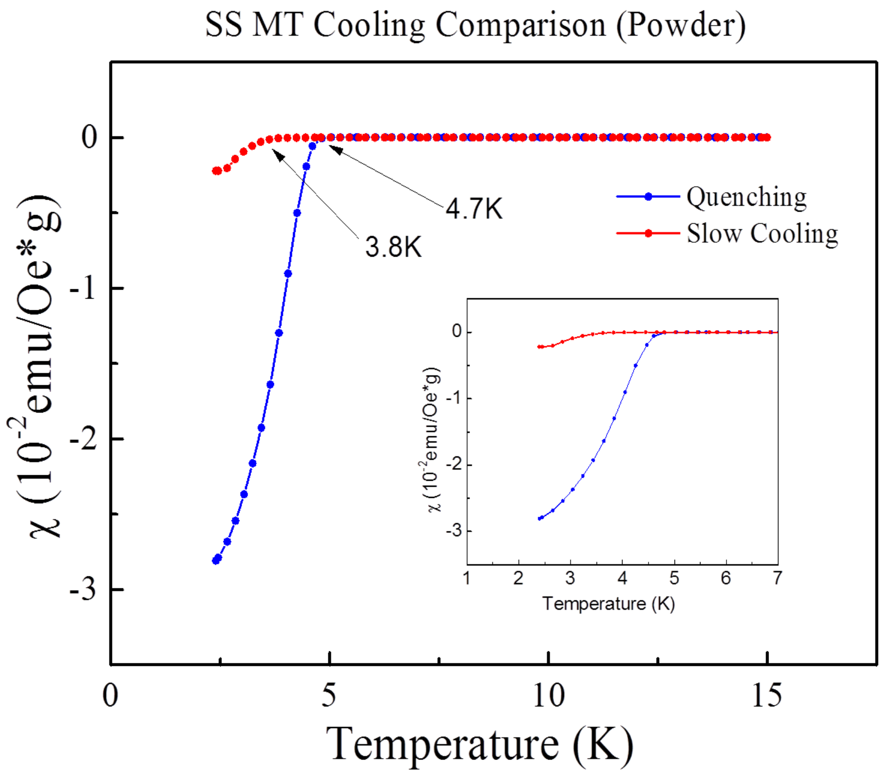


Figure 14. Magnetic susceptibility graph of different cooling condition

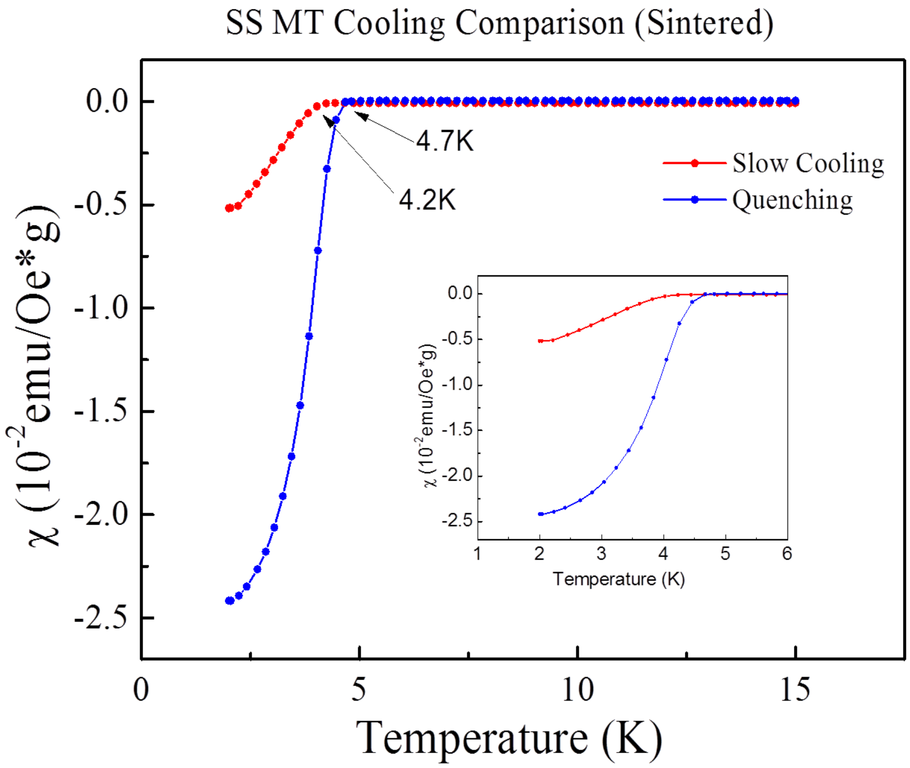


Figure 15. Magnetic susceptibility graph of different cooling condition

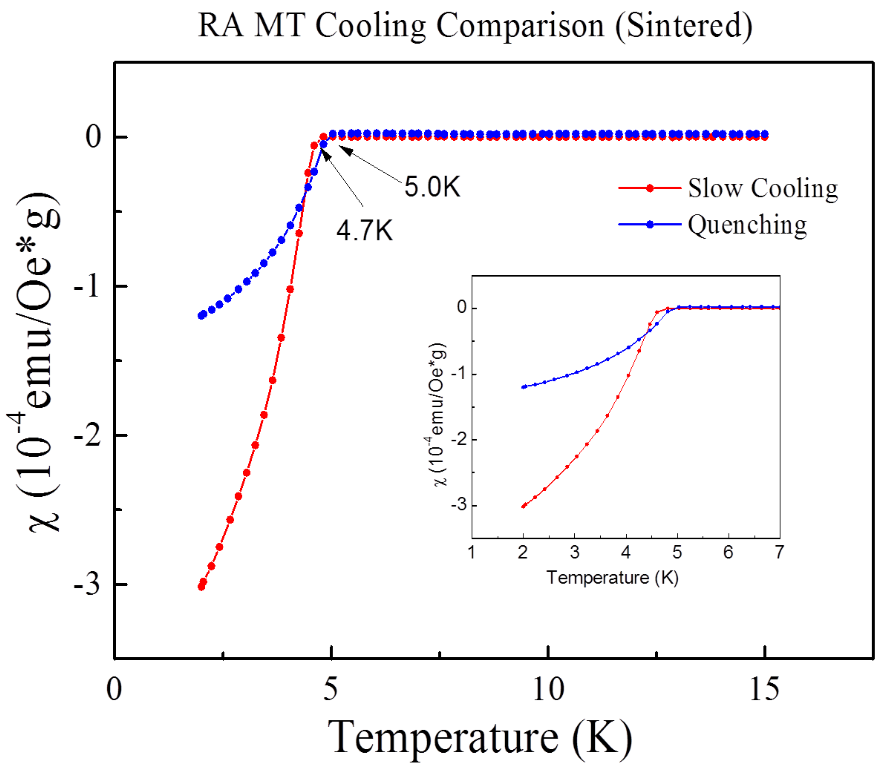


Figure 16. Magnetic susceptibility graph of different cooling condition

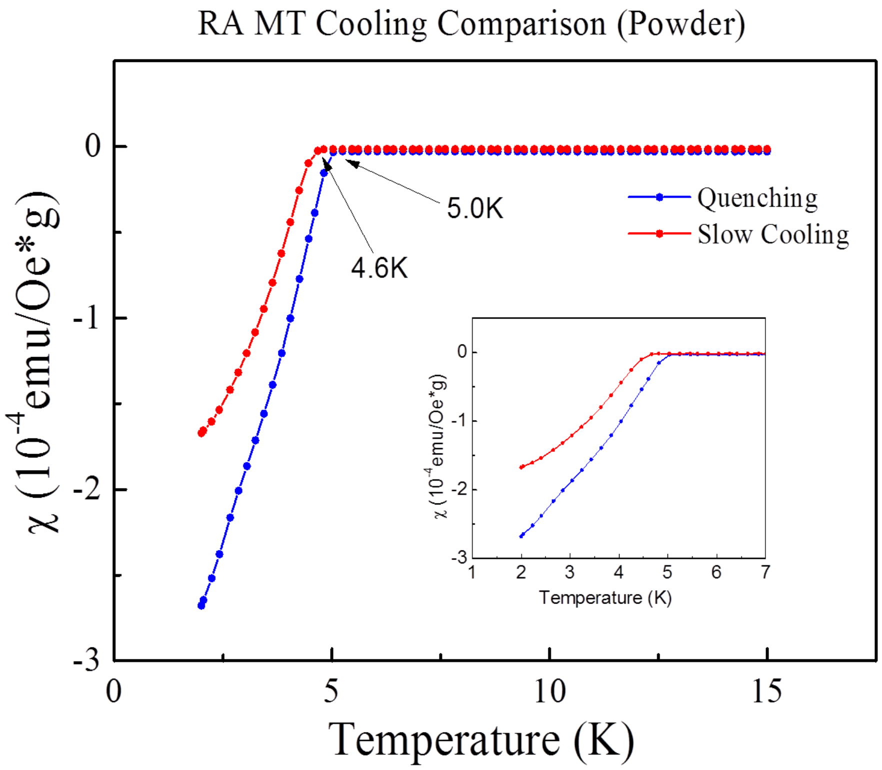


Figure 17. Magnetic susceptibility graph of different cooling condition

High Pressure Synthesis:

As said before, high pressure synthesis have rather similar result with both slow cooling and quenching, powder and sinter.

Solid State Reaction Method:

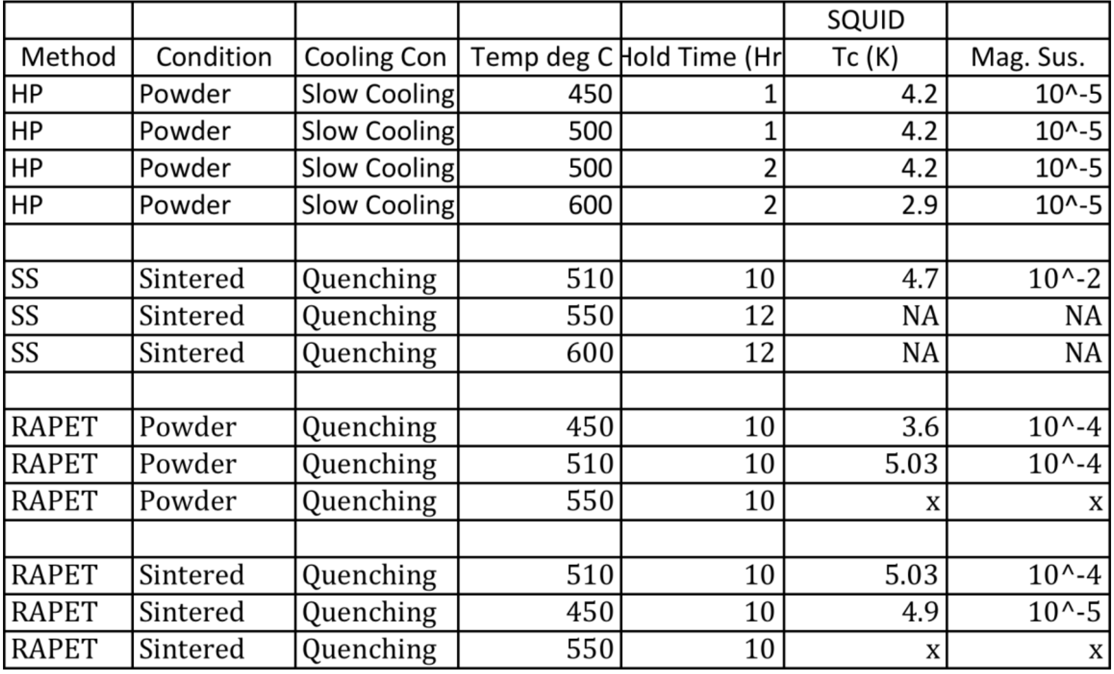
By comparing solid state reaction method, quenching seem to improve both T_c, and magnetic susceptibility. T_c has an increase of almost 1K maximum while magnetic susceptibility of quenching is about 10 times the slow cooling, which means that the superconductivity percentage increases drastically.

RAPET:

T_c of quenching method is about 0.4K higher than T_c of slow cooling method. The maximum magnetic susceptibility change of quenching to slow cooling has 10 times difference where quenching method samples have larger magnetic susceptibility.

4. Testing Temperature Condition of Different Methods

Table 5. Temperature condition variation results



					SQUID	
Method	Condition	Cooling Con	Temp deg C	Hold Time (Hr	Tc (K)	Mag. Sus.
HP	Powder	Slow Cooling	450	1	4.2	10^-5
HP	Powder	Slow Cooling	500	1	4.2	10^-5
HP	Powder	Slow Cooling	500	2	4.2	10^-5
HP	Powder	Slow Cooling	600	2	2.9	10^-5
SS	Sintered	Quenching	510	10	4.7	10^-2
SS	Sintered	Quenching	550	12	NA	NA
SS	Sintered	Quenching	600	12	NA	NA
RAPET	Powder	Quenching	450	10	3.6	10^-4
RAPET	Powder	Quenching	510	10	5.03	10^-4
RAPET	Powder	Quenching	550	10	x	x
RAPET	Sintered	Quenching	510	10	5.03	10^-4
RAPET	Sintered	Quenching	450	10	4.9	10^-5
RAPET	Sintered	Quenching	550	10	x	x

We made assumptions in prior about temperature conditions that all methods have about the same range of best temperature conditions. But this assumption has to be verified.

High pressure synthesis tends to have a larger temperature range larger than 600 degrees Celsius where superconductivity still exists. Whereas Solid State and RAPET method has a small range that superconductivity exists, which is at least less than 550 degrees Celsius. This may be cause by the lack of sulfur in RAPET and solid state reaction method.

One of the advantages of high pressure synthesis is that it protects sulfur from leaving the sample, while RAPET and solid state method doesn't. Sulfur would be able to diffuse out of the sample into the tube for RAPET method, while it may also leave the sample into the quartz tube for solid state reaction method. A way to determine whether this hypothesis may be true is by EDX data and XRD.

5. Doping of other BiS_2 layered superconductors $Bi_4Se_4S_3$ and $Bi_4Te_4S_3$

I've tried doping other materials such as $Bi_4Se_4S_3$ and $Bi_4Te_4S_3$ to see if other BiS_2 based compounds might also be superconductors. But results have shown that $Bi_4Se_4S_3$ and $Bi_4Te_4S_3$ do not have superconductivity, probably because of the cause of having a much larger atomic scale so that the compound crashes.

(II). Chemical Analysis

By using EDX to find the mass percentage of Bi, O, and S, we are able to figure out the ratio to see whether the three elements are in their 4:4:3 ratio. By Mass percentage/atomic weight, we would be able to get the molecular percentage. Then, turn it into a ratio to have a comparison with the 4:4:3. The pictures and data below are a few of the chemical analysis of $Bi_4O_4S_3$.

High Pressure Synthesis SEM Pictures and EDX Data

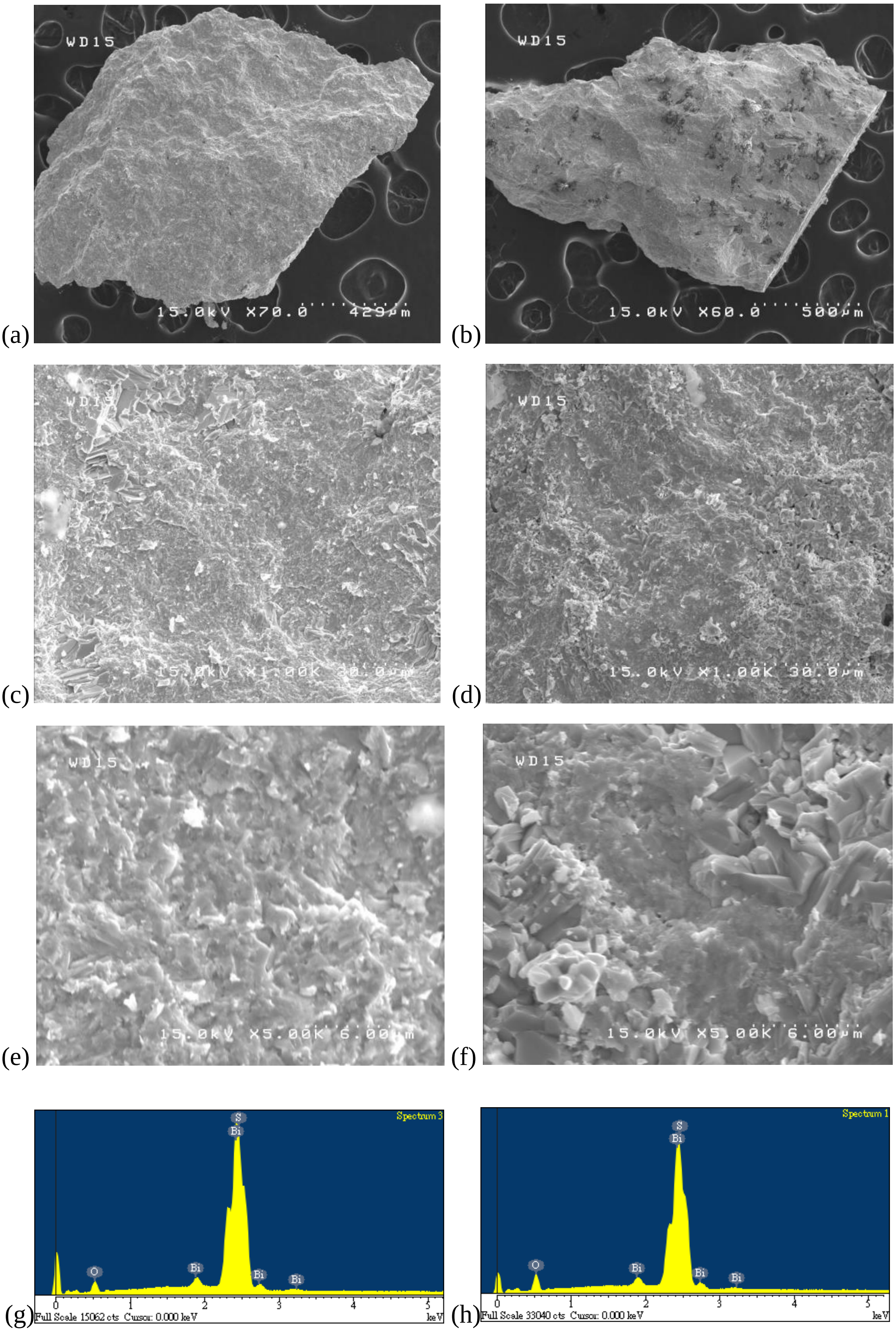
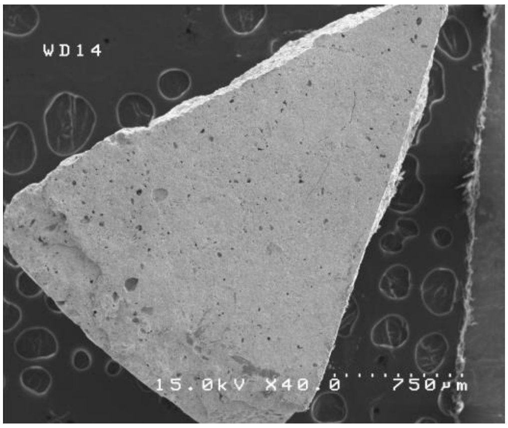


Figure 18. (a) (b) (c) (d) (e) (f) SEM images of HP (g) (h) EDX data of HP

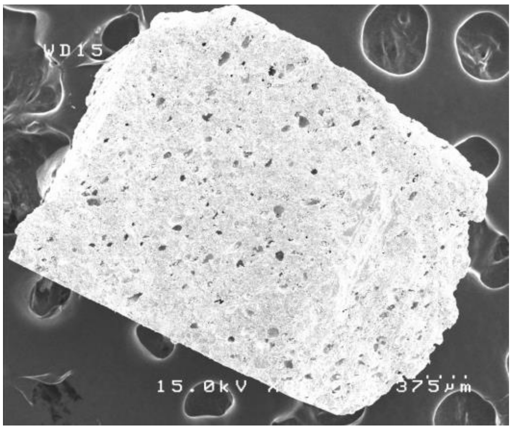
Table 6. HP EDX table

BOS4_1					
element	atomic weight	mass%	mol%	total	real rate
Bi	208.98037	80.62	0.38577786	1.32678527	0.29076134
O	16	10.75	0.671875	1.32678527	0.50639317
S	32.066	8.63	0.26913241	1.32678527	0.20284549
BOS9_1					
element	atomic weight	mass%	mol%	total	real rate
Bi	208.98037	82.91	0.39673583	1.26006517	0.31485342
O	16	10.55	0.659375	1.26006517	0.52328643
S	32.066	6.54	0.20395434	1.26006517	0.16186016

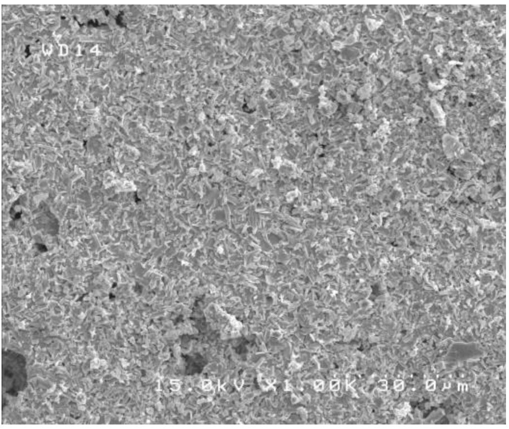
Solid State Reaction Method of SEM Pictures and EDX Data



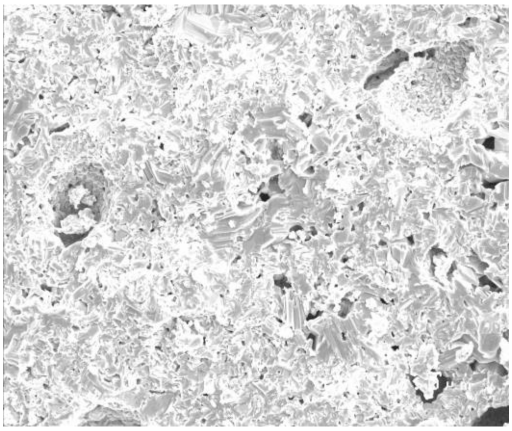
(a)



(b)



(c)


(d)

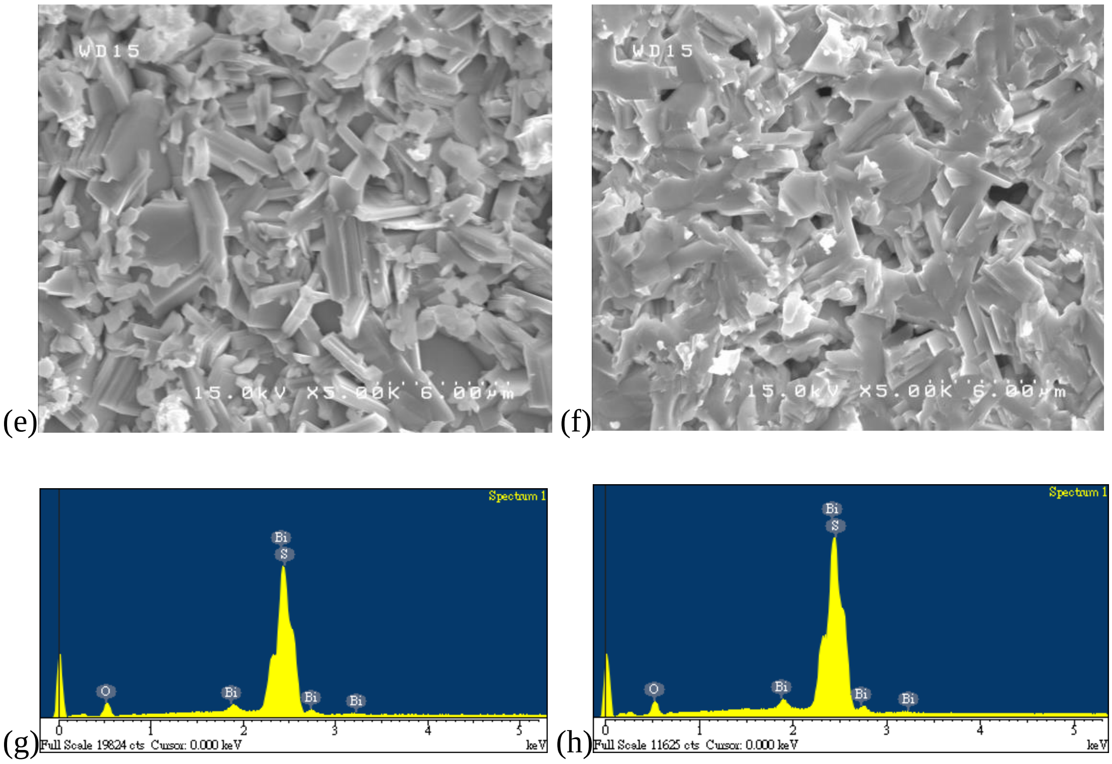


Figure 19. (a) (b) (c) (d) (e) (f) SEM images of SS (g) (h) EDX data of SS

Table 7. SS EDX table

BOS7_1					
element	atomic weight	mass%	mol%	total	real rate
Bi	208.98037	82.38	0.3941997	1.23804599	0.31840473
O	16	9.4	0.5875	1.23804599	0.47453811
S	32.066	8.22	0.25634629	1.23804599	0.20705716
BOS11_1					
element	atomic weight	mass%	mol%	total	real rate
Bi	208.98037	82.57	0.39510888	1.19576713	0.33042293
O	16	8.22	0.51375	1.19576713	0.42964051
S	32.066	9.2	0.28690825	1.19576713	0.23993656

RAPET TEM Pictures and EDX Data

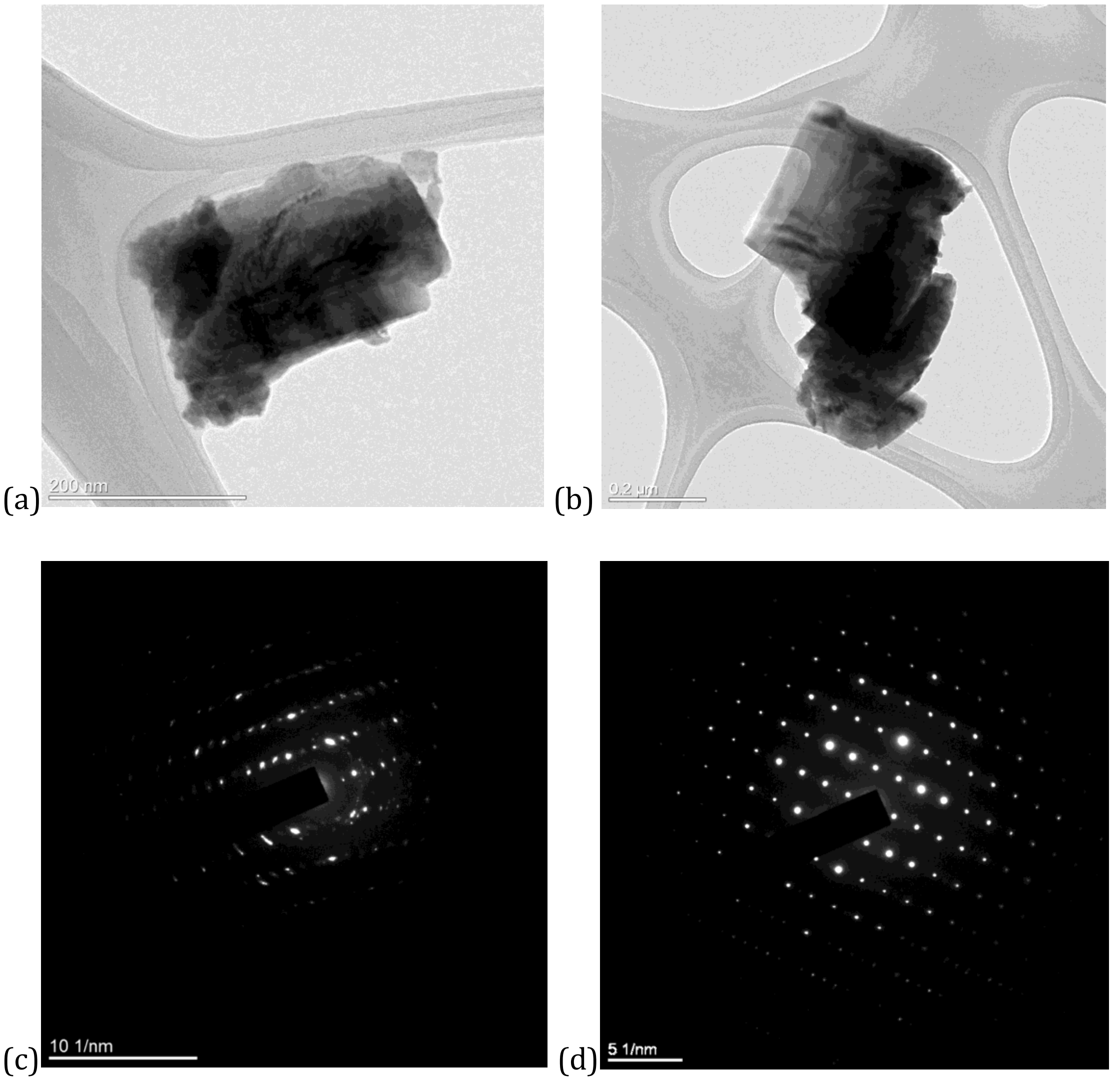


Figure 20. (a) (b) (c) (d) TEM images of RA

Table 8. RA EDX table

RBOS1_2					
element	atomic weight	mass%	mol%	total	real rate
Bi	208.98037	84.9	0.40625825	0.9031529	0.44982223
O	16	0.83	0.051875	0.9031529	0.05743767
S	32.066	14.27	0.44501965	0.9031529	0.4927401
RBOS2_1					
element	atomic weight	mass%	mol%	total	real rate
Bi	208.98037	91.03	0.43559115	0.74476344	0.58487182
O	16	0.95	0.059375	0.74476344	0.0797233
S	32.066	8.01	0.24979729	0.74476344	0.33540488

By the pictures above, we would be able to tell that the difference between two types of SEM pictures by high pressure synthesis and solid state reaction method. High pressure synthesis samples are rougher surface than solid state reaction method samples. But both samples seem to be uniformly synthesized by the two methods. Seems like the rougher sample would have lower T_c than the smoother one.

By looking at the TEM samples of RAPET, it shows that RAPET samples are at about hundered nanometers in scale. That is much smaller than the two SEM samples above. The two pictures show that the sample is layered structure by its rectangular form. Therefore, the reason which RAPET have a higher T_c is caused by the sample being nano-scale.

Since the smoothness of the sample may effect its T_c,, then another method should be introduced. Through film making, the sample should be completely smooth, and change our polycrystalline sample into monocrystalline. Through XRD, it shows that the peaks of polycrystalline sample did become less in quantity, but did not turn into a monocrystalline. Tried several times, but was not able to change it into a monocrystaline to see if there might be possible changes in T_c.

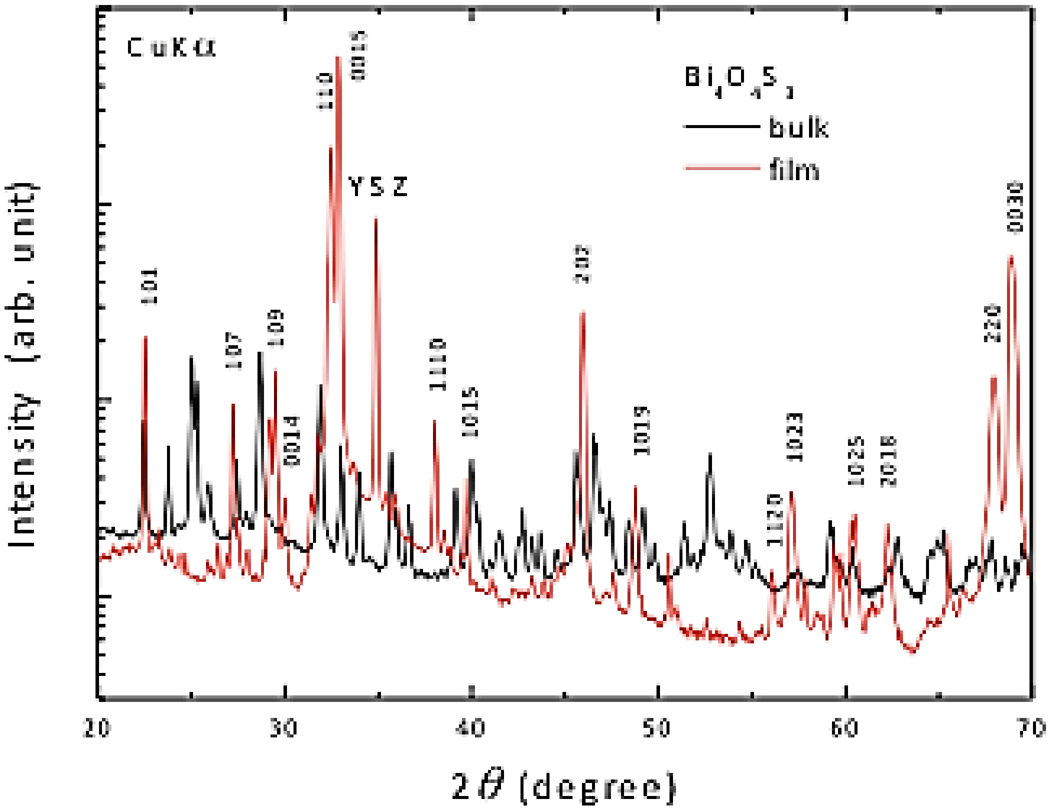
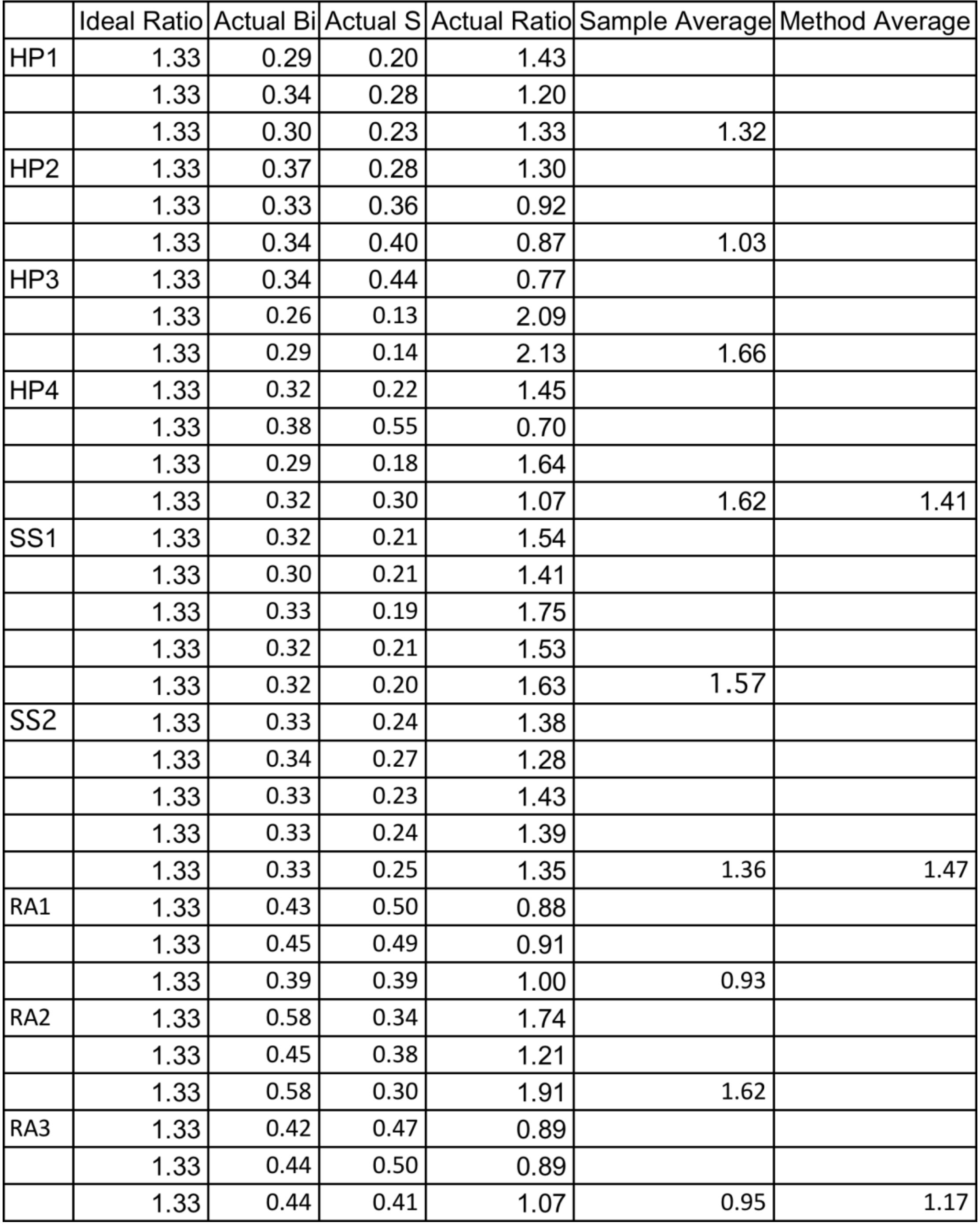


Figure 21. Bulk and PLD XRD results

Table 9. EDX results analysis



	Ideal Ratio	Actual Bi	Actual S	Actual Ratio	Sample Average	Method Average
HP1	1.33	0.29	0.20	1.43		
	1.33	0.34	0.28	1.20		
	1.33	0.30	0.23	1.33	1.32	
HP2	1.33	0.37	0.28	1.30		
	1.33	0.33	0.36	0.92		
	1.33	0.34	0.40	0.87	1.03	
HP3	1.33	0.34	0.44	0.77		
	1.33	0.26	0.13	2.09		
	1.33	0.29	0.14	2.13	1.66	
HP4	1.33	0.32	0.22	1.45		
	1.33	0.38	0.55	0.70		
	1.33	0.29	0.18	1.64		
	1.33	0.32	0.30	1.07	1.62	1.41
SS1	1.33	0.32	0.21	1.54		
	1.33	0.30	0.21	1.41		
	1.33	0.33	0.19	1.75		
	1.33	0.32	0.21	1.53		
	1.33	0.32	0.20	1.63	1.57	
SS2	1.33	0.33	0.24	1.38		
	1.33	0.34	0.27	1.28		
	1.33	0.33	0.23	1.43		
	1.33	0.33	0.24	1.39		
	1.33	0.33	0.25	1.35	1.36	1.47
RA1	1.33	0.43	0.50	0.88		
	1.33	0.45	0.49	0.91		
	1.33	0.39	0.39	1.00	0.93	
RA2	1.33	0.58	0.34	1.74		
	1.33	0.45	0.38	1.21		
	1.33	0.58	0.30	1.91	1.62	
RA3	1.33	0.42	0.47	0.89		
	1.33	0.44	0.50	0.89		
	1.33	0.44	0.41	1.07	0.95	1.17

The reason that we do not calculate the oxygen is because most likely, the oxygen percentage would be off because EDX does not detect lighter elements well. Therefore we exclude oxygen and find the ratio of Bismuth and Sulfur.

The method with the closest ratio of the $Bi_4O_4S_3$ ratio is the high pressure method. The ratio is 1.41 while the others are 1.47 and 1.17. Since high pressure is a closed system where sulfur hardly gasify, the ratio of $Bi_4O_4S_3$ tend to remain closer to the ideal ratio. This would be the advantage of using high pressure synthesis, but on the contrary it seems like the high pressure samples are not uniformly distributed. Each point has its distinguish ratio but the average is quite close to 4:3. The possible reason would be the holding time at temperature around 500 degrees Celsius is not long enough, so that the chemicals are not evenly distributed.

IV. Discussion

(I). Tri-layered $Bi_4O_4S_3$

1. Structure Analysis

It has been reported recently, that $Bi_4O_4S_3$ is a new BiS_2-based layered structure superconductor. The crystal structure analysis shows that $Bi_4O_4S_3$ is crystalized in a tetragonal structure that has the space group of I4/mmm. This layered structure new material is composed of stacking layers of BiS_2, Bi_2O_2, and SO_4 layers. The lattice parameters have the value of a=3.9697 Angstrom and c=41.3520 Angstrom.

The picture below shows the structure of $Bi_4O_eS_3$ in a layered form. By using Crystal Maker to generate the atomic structure of $Bi_4O_eS_3$ we would be able to visualize the structure and analyze for possible doping elements. XRD could also be generated by this program and compared to the actual data we've measured. Through checking a few highest peaks, the structure I've put together would be close to the actual $Bi_4O_4S_3$.structure.

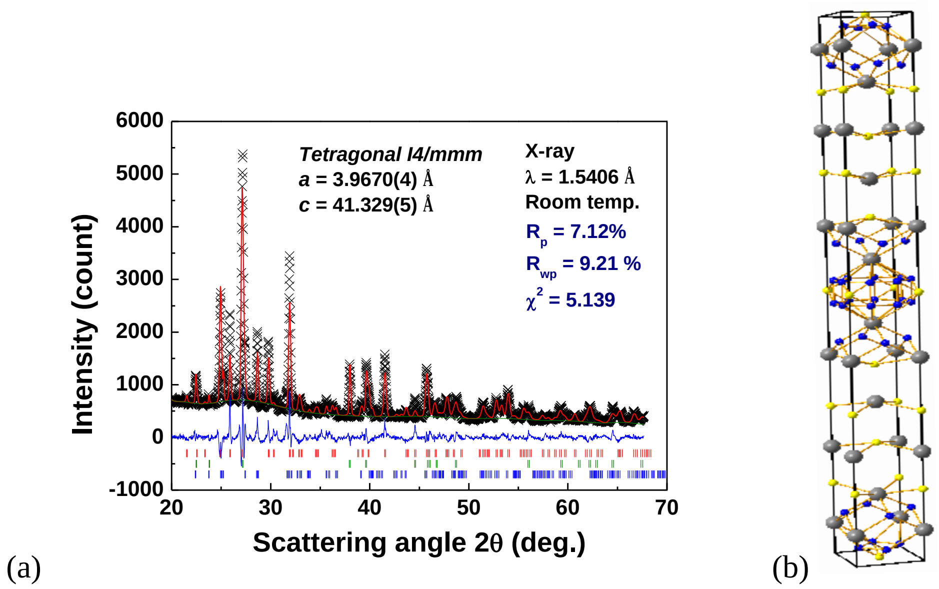


Figure 22. (a) X-ray diffraction pattern of $Bi_4O_4S_3$ at room temperature (b) Crystalline structure of $Bi_4O_4S_3$

2. Superconducting Parameters

Effects of reaction temperature

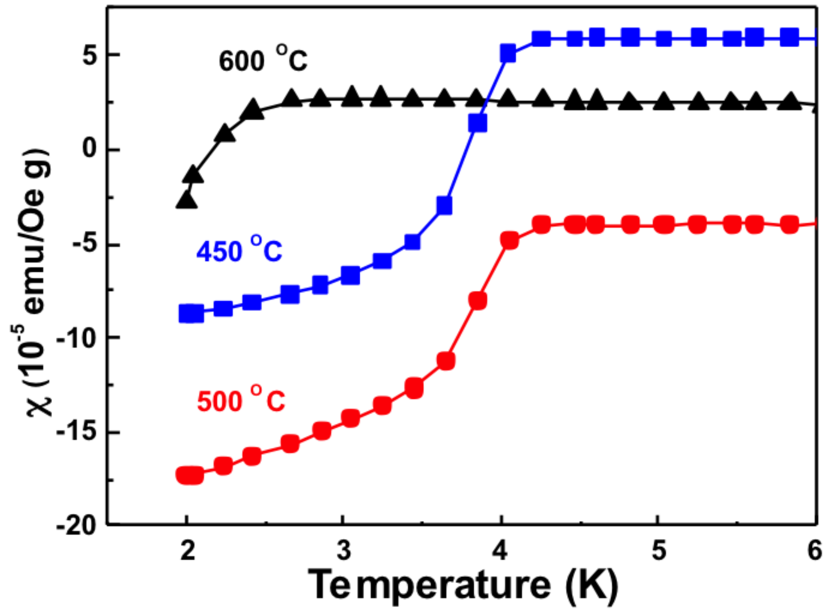


Figure 23. Direct comparisons of superconducting diamagnetic responses of the three HP samples

This figure shows the magnetic susceptibility of various samples synthesized at different temperature by using high pressure synthesis along with slow cooling method. The critical temperature of the sample fabricated at 600°C is significantly lower than the other two. The paramagnetic responses of the sample fabricated at 450°C are considerably higher. Therefore, a synthesizing temperature of 500°C can generate the best superconducting characters. Therefore chosen this as the synthesizing temperature.

Effects of reaction process

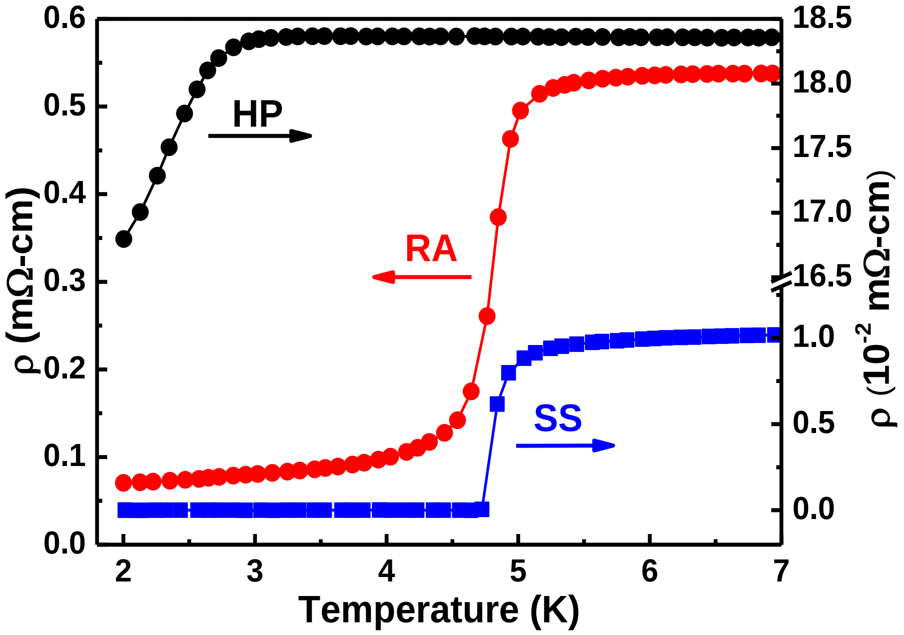


Figure 24. Direct comparisons of the resistivity curves of the HP, SS, and RA samples

The figure shows the Resistivity to temperature curves of samples fabricated using different methods using 500°C fabrication temperature with rapid quenching. The resistivity measurements show that superconductivity does develop in all three samples due to their extreme drops showing diamagnetism. Among all data curves, RA method appears to generate the highest T_C. With RA sample reaching 4.9 K, it is 11% higher than the reported one. Therefore, in the three methods RA method was chosen as the method with best superconducting properties. After examining the differences of slow cooling and quenching method with the RA synthesizing method, it is proven that RA method at 500°C fabrication temperature with rapid quenching appears to have the best superconducting character.

Effects of reaction process

This figure shows the direct comparison of the (0 0 12) reflections of the slow cooling and rapid quenching samples. Whereas the numbers below represent the full width half maximum of the two peaks. The width of x-ray diffraction peak of the rapid quenching sample is 16% broader than that of the slow cooling one, which can be resulted from either finite size effect or from chemical disorder.

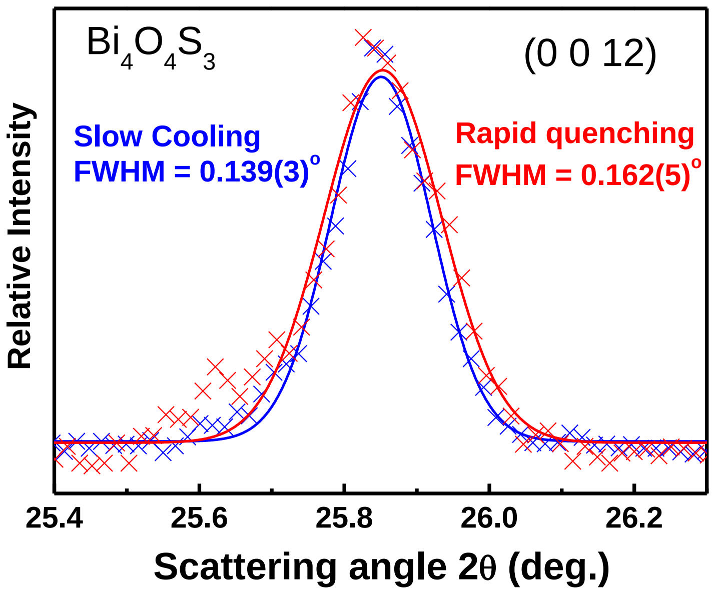


Figure 25. A direct comparison of the (0 0 12) reflections of the SC and RQ samples.

The TEM images show that the resultant crystals in both samples are around 200 nm in diameter, indicating that finite size effect plays no major role. Since, finite size effects that affects the broadness of peaks should be sizes below 30 nm.

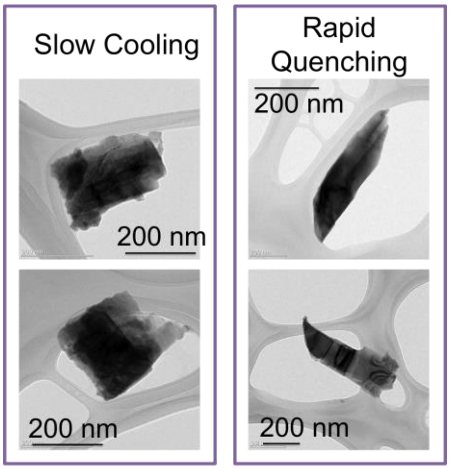
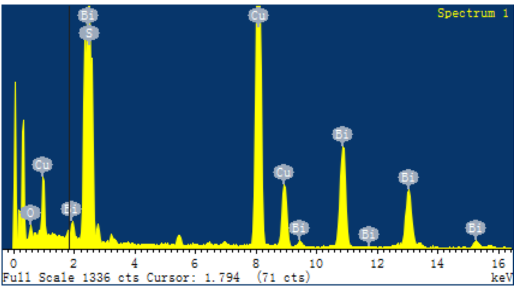


Figure 26. TEM images of the crystals fabricated through SC or RQ process

This EDX spectrum is an example of what indicates the atomic ratio of samples. On this table, it indicates that rapid quenching method appears to be highly sulfur deficient of 15%.

(a)


(b)

Bi : S ratio	
Slow cooling	1 : 1.08
Rapid quenching	1 : 0.63

Figure 27. (a) A representative EDX spectrum of the RQ sample (b) Bi:S ratio chart

$\chi(T)$ of both samples can be described by London equation to give T_C of 4.6 and 4.9K for the slow cooling and rapid quenching samples, respectively. Surprisingly, chemical disorder gives rise to a noticeably higher critical temperature. By using London equation, pairing parameters of $\alpha=3.1$ and 2.6 were obtained for the rapid quenching and slow cooling samples, respectively, which are considerably larger than the $\alpha=2$ expected for the BCS-type of pairings. Relatively long penetration depths were also obtained for both samples.

$$\lambda = \frac{\lambda_0}{\sqrt{1-\left(\frac{T}{T_C}\right)^{\alpha}}} \qquad \chi = \chi_0 - c\left(\frac{3}{2\rho}\right)\left\{1-\left[\left(\frac{3\lambda}{R}\right)\left(\frac{1}{\tanh\frac{R}{\lambda}}\right)+3\left(\frac{\lambda}{R}\right)^2\right]\right\}$$

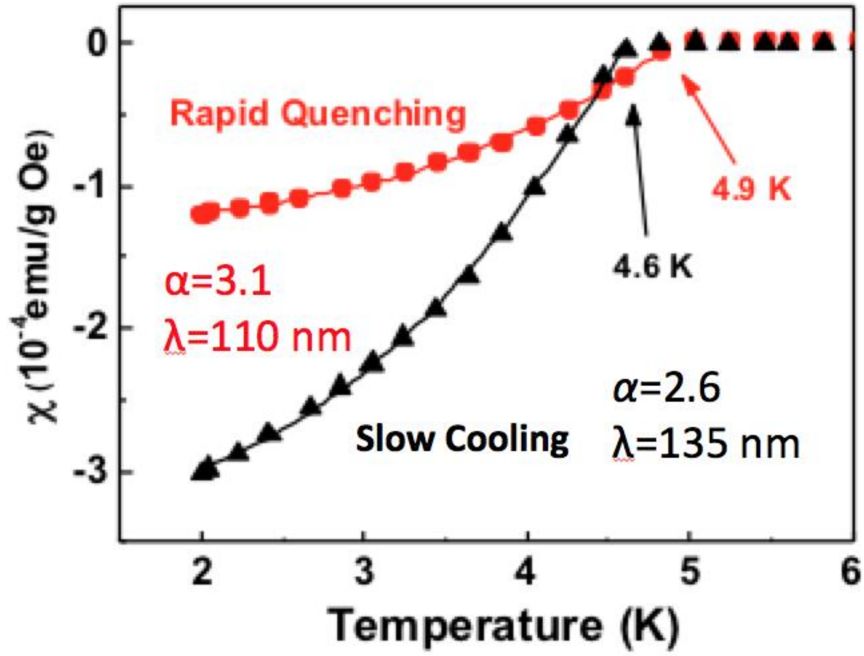


Figure 28. χ (T) of the SC and RQ samples

Type-II M(H) curves were observed for both samples. The critical magnetic fields of the RQ sample reach $H_{C1}\sim$60 Oe and $H_{C2}\sim$2.9 kOe. Which there is a rather large difference between H_{C1} and H_{C2} in comparison to BCS type superconductors.

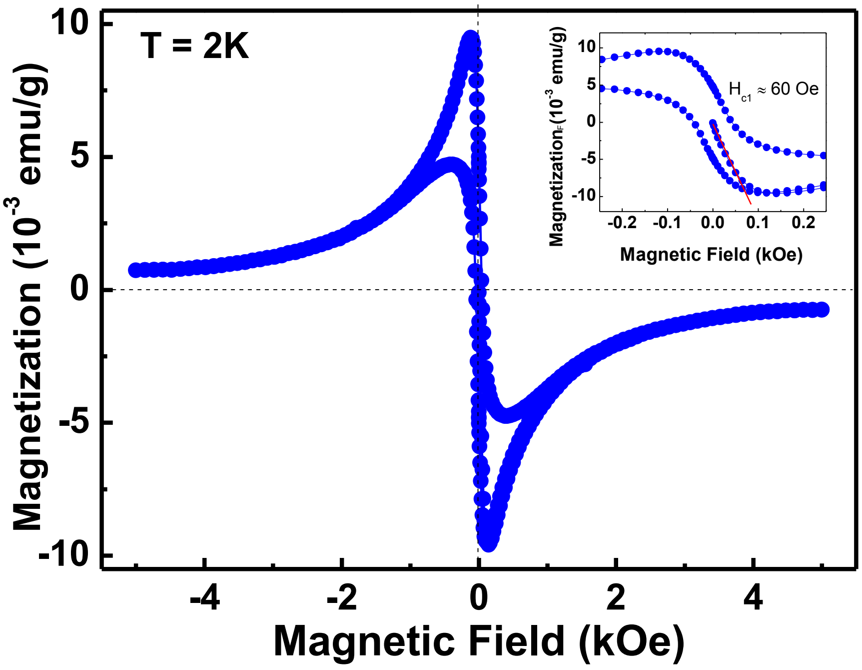


Figure 29. M(H) curve of the RQ sample

(II). Bi-layered $LaOBiS_2$

$LaOBiS_2$ crystalizes into a bi-layered tetragonal structure. Recent reports [3,4] indicate that superconductivity does not develop in the samples fabricated using SS and HP methods with temperature reduced to 1.8K.

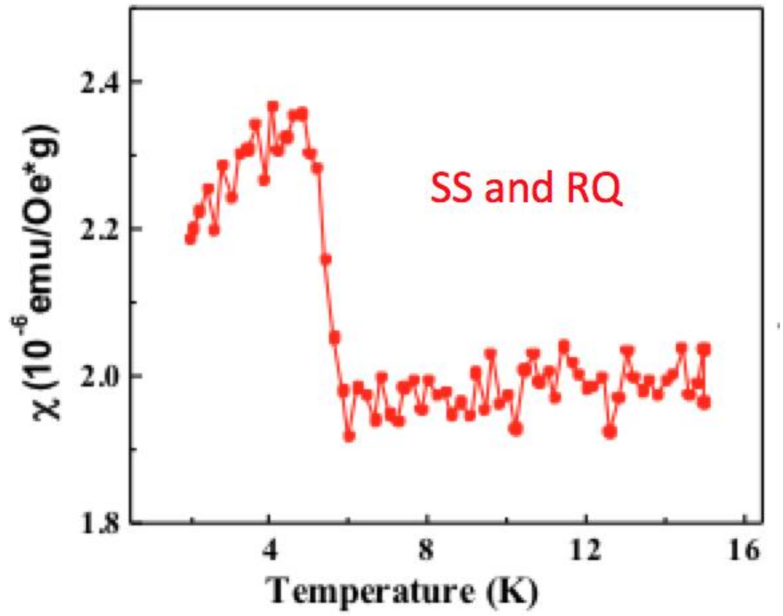
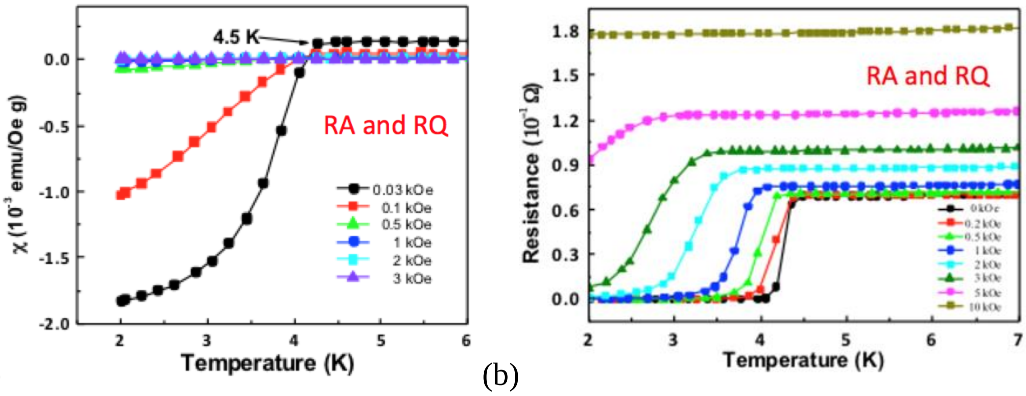


Figure 30. χ (T) curve of the SS with RQ sample

Both of the resistivity and magnetic susceptibility measurements reveal the appearance of the superconductivity below 4.5 K by RA method with rapid quenching. No sign of superconductivity was observed in the SS with RQ sample of Bi:S=1:2. Superconductivity below 4.5 K is indeed found in the RA with RQ sample, where significant Bi-deficiency of Bi:S=0.8:2 was detected.



(a) (b)

Figure 31. (a) χ (T) curve of the RA with RQ sample (b) Resistance curve of the RA with RQ sample

V. Conclusions

By using different methods, we are able to increase T_c, magnetic susceptibility, resistivity, and change the particle dimensions of a $Bi_4O_4S_3$ sample. By analyzing samples in different time, temperature, pressure, cooling conditions and chemical compounding conditions, we are able to find the best condition for different purposes.

This experiment analyzes some effective condition approaches that people could possibly use when dealing with a new material. Besides from the general point of view, through EDX, high pressure synthesis keeps Sulfur from gasifying, which lets $Bi_4O_4S_3$ remain at about the same ratio. RAPET method locks the chemicals in the switch lock, which synthesizes the chemicals uniformly. Samples with highest T_c is made by the RAPET method turning the sample into nano scale may enhance T_c.

Results show that chemical disorder created by RAPET or by rapid quenching plays an effective role in the development of superconductivity in BiS2-based oxides. A 15% S-deficiency in tri-layered Bi4O4S3 created by RAPET with rapid quenching raises the superconducting TC by 11%. Surprisingly, superconductivity does appear in the bi-layered LaOBiS2 created by RAPET with rapid quenching. A 25% Bi-deficiency was observed in the sample, which triggered the development of superconductivity.

VI. References

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