行政院國家科學委員會專題研究計畫　成果報告

子計畫三：釔氧 2116 系相圖鎢氧化物與製程之研究

計畫類別： 整合型計畫
計畫編號： NSC92-2112-M-032-022-
執行期間： 92 年 08 月 01 日至 94 年 01 月 31 日
執行單位： 淡江大學物理學系

計畫主持人： 錢凡之

報告類型： 完整報告

處理方式： 本計畫可公開查詢

中　華　民　國 94 年 6 月 27 日

行政院國家科學委員會補助專題研究計畫成果報告

（計畫名稱）

新穎過渡金屬氧化物之研究(3/3)

子計畫三：釩氧 2116 系相圖鎢系氧化物與製程之研究

計畫類別：□ 個別型計畫　　■ 整合型計畫
計畫編號：NSC　92－　2112　－M　－　032 －022　　－
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成果報告類型(依經費核定清單規定繳交)：■精簡報告　□完整報告

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執行單位：淡江大學物理系

中　華　民　國　94　年　6　月　27　日

一、中文摘要

我們以固態法燒結的四元化合物 $Bi_XPb_YWO_3$。其中當 $x \leq 0.15$ 與 $y \leq 0.35$ 之時，樣品之 Meissner 效應與電阻率的行為顯示了 8.7 K 的超導。經過 X-ray 的粉末繞射分析，此樣品之主要結晶相可以暫定為空間群為 P4/mbm 的立方結構，如同其母體 $Pb_{0.26}WO_3$，而其晶格常數則為 $a = b = 12.220$ Å, $c = 3.784$ Å。

關鍵詞：超導、黃鐵礦、立方晶系。

英文摘要

Quaternary tungsten bronze $Bi_XPb_YWO_3$ with $x \leq 0.15$ and $y \leq 0.35$, synthesized through solid state reaction method, is found to be superconducting at 8.7 K with consistent Meissner effect and resistivity measurements. Through X-ray powder diffraction analysis, the major phase of the bulk sample is tentatively assigned to a tetragonal crystalline structure of space group P4/mbm, as that of its parent compound $Pb_{0.26}WO_3$, with $a = b = 12.220$ Å, $c = 3.784$ Å.

KEY WORDS: superconductors, tungsten bronze, tetragonal.

1. INTRODUCTION

The nonstoichiometric compounds M_XWO_3 (where M represents an alkali atom) , commonly referred as the alkali tungsten bronzes, were discovered to be superconducting with transition temperature T_C ranging from 0.55 to 7 K by Mathias et al. in 1964 [1]. Many studies were centered mainly on the cubic Na_XWO_3 with $0.5 < x < 1.0$ [2, 3], which has an insulating parent compound in WO_3 with building blocks of WO_6 octahedron. Na_XWO_3 is not superconducting in its tetragonal phases as $x < 0.5$. In this study we report the finding of superconductivity in tetragonal tungsten bronze $Bi_XPb_YWO_3$ with $x \leq 0.15$ and $y \leq 0.35$ at 8.7 K.

2. EXPERIMENTS

Samples investigated were prepared by the solid state reaction method. The proper stoichiometric amounts of high purity powders of Bi_2O_3, PbO, WO_3 and W were thoroughly mixed and ground, then pressed into pellets. The pellets were calcined in Al_2O_3, crucibles at 800 ℃ for 5 hrs in flowing Ar atmosphere. Subsequently samples were grounded, pressed and fired at 800 ℃ again for another 5 hrs in flowing Ar atmosphere. The room temperature powder x-ray measurements were carried out using $Cuk_{\alpha 1}$ radiation (λ =1.5406 Å) monochromatized by Ge (111) crystal from Rigaku 12 kW RU200 x-ray generator. Intensity data were collected over a 2θ range from 20° to 60° at a step width of 0.02°. Dc magnetization measurements were performed with a SQUID magnetometer (MPMSR2,

Quantum Design) which was previously calibrated using a lead sample with T_C of 7.2 K. The standard four-probe technique was carried out using PPMS for resistivity measurements.

3. RESULTS AND DISCUSSIONS

Figure 1 shows the magnetization curves of the composite sample $Bi_{0.15}Pb_{0.35}WO_3$ as a function of temperature from 4 K to 20 K, under conditions of zero field cooling (ZFC) and field cooling (FC) at 10 Oe. The existence of the superconducting phase was confirmed unambiguously by measuring the Meissner effect with onset T_C at 8.7 K. A superconducting volume fraction of 30% under a magnetic field of 10 Oe was obtained at 4 K, indicating that the superconductivity is bulk in nature and originated from $Bi_XPb_YWO_3$.

Figure 2 shows the temperature dependence of the resistivity of the composite sample $Bi_{0.15}Pb_{0.35}WO_3$ from 4 K to 20 K under zero magnetic field. The onset transition temperature is 8.7 K and zero resistivity 8.6 K.

Figure 3 shows the x-ray powder diffraction pattern of the sample $Bi_{0.15}Pb_{0.35}WO_3$ taken at room temperature with 2θ range from 20° to 60°. The dominant phase in $Bi_XPb_YWO_3$ with $x \leq 0.15$ and $y \leq 0.35$ are indexed based on a tetragonal crystalline structure of space group P4/mbm, as that of its parent compound $Pb_{0.26}WO_3$ [4, 5, 6], with a = b = 12.220 Å, c = 3.784 Å. There are a few extra peaks. Through investigating various samples the Bragg peaks at 2θ = 27.18°, 37.94°, and 39.70° are identified to be Bi (102), (104), and (110) respectively. And 40.26° is W (110). At least two peaks at 30.84° and 33.30°, indicated by the arrows, are not yet identified. With the discrepancy in the x-ray powder patterns the exact chemical composition of the superconducting compound was not able to be determined.

To summarize, the superconductivity at 8.7 K was truly realized in this compound $Bi_{0.15}Pb_{0.35}WO_3$, which may take a tetragonal crystalline structure as that of $Pb_{0.26}WO_3$.

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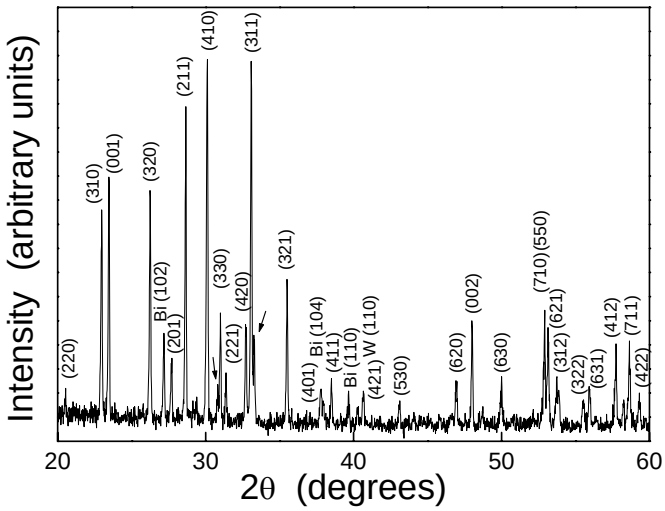
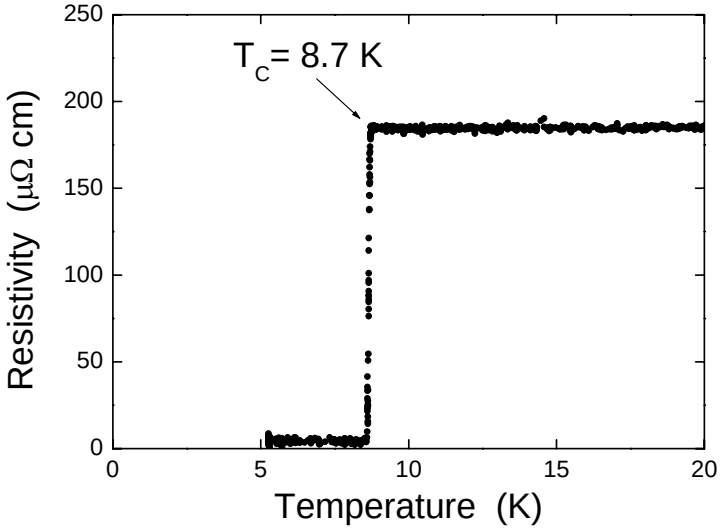
Figure captions

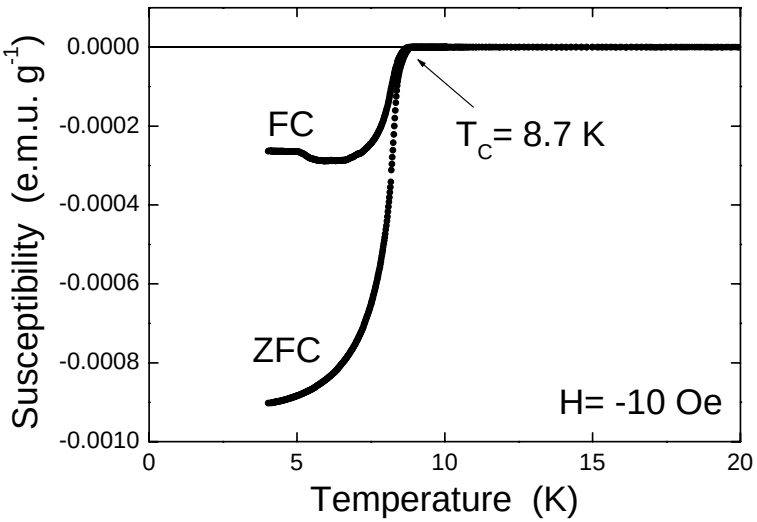
Fig. 1. Magnetization of the sample $Bi_{0.15}Pb_{0.35}WO_3$ as a function of temperature under conditions of zero field cooling (ZFC) and field cooling (FC) at 10 Oe.

Fig. 2. Temperature dependence of the resistivity of the sample $Bi_{0.15}Pb_{0.35}WO_3$ under zero magnetic field.

Fig. 3. The room temperature x-ray diffraction patterns of the sample $Bi_{0.15}Pb_{0.35}WO_3$ using $Cuk_{\alpha 1}$ radiation (λ =1.5406 Å) with 2θ ranging from 20° to 60°.


Intensity (arbitrary units)
2θ (degrees)
20
30
40
50
60
(220)
(310)
(001)
(320)
Bi (102)
(201)
(211)
(410)
(330)
(221)
(420)
(311)
(321)
(401)
Bi (104)
(411)
Bi (110)
W (110)
(421)
(530)
(620)
(002)
(630)
(710)
(550)
(621)
(312)
(322)
(631)
(412)
(711)
(422)


Resistivity (μΩ cm)
Temperature (K)
T_C = 8.7 K
0
50
100
150
200
250
0
5
10
15
20


Susceptibility (e.m.u. g-1)
0.0000
-0.0002
-0.0004
-0.0006
-0.0008
-0.0010
0
5
10
15
20
Temperature (K)
FC
ZFC
Tc= 8.7 K
H= -10 Oe