TECHNICAL ARTICLE

Investigations on ancient bronze drums from Majiang, Guangxi, P. R. China

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Six different types of Majiang bronze drums from Hechi City, Guangxi, China were collected from the Guangxi Museum to characterize the original scheme of polychromy and materials used for the drums. The composition of all the samples were determined by using scanning electron microscopy with energy-dispersive X-ray spectroscopy. All the bronze drums contain mainly Cu, Sn, Pb, and As. Qualitative analysis of the structure by X-ray powder diffraction indicates that each of the six bronze drums contains four or five phases, namely (Cu, As), Pb, Cu_3Sn, and $Cu_{10}Sn_3$ or Cu, Pb, $As_{0.2}Cu_{1.8}$, Cu_3Sn, and $Cu_{10}Sn_3$. The Rietveld structural refinement is performed first time for the quantitative analysis of ancient bronze drums and inorganic cultural relics. This paper reports the result.

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Key words: ancient bronze drums, alloys, powder X-ray diffraction, crystal structure, Rietveld refinement

I. INTRODUCTION

The bronze drum is a bronze artistic treasure created by the ethnic minorities in southern China. In ancient times, the bronze drum was not only a heavy instrument symbolizing power and wealth, but also had social functions such as offering sacrifices to gods, commanding army formations, transmitting information, and celebrating entertainment (Qin and Wan, 2005). Since the Wanjiaba-type bronze drum was discovered in Yunnan Province more than 2700 years ago, the bronze drum and its culture have continuously developed and evolved, and gradually became popular in Southwest China and Lingnan region, and spread to most countries in Southeast Asia, forming the so-called bronze drum culture circle (Feng, 1974; Li et al., 1992; Shuyun et al., 2005). Lingnan region is a geographic area referring to the lands in the south of the Nanling Mountains. The region covers the modern Chinese subdivisions of Guangdong, Guangxi, Hainan, Hong Kong & Macau, and the Northern half of Vietnam. In the 1980s, scientific and technological archaeological researchers of the bronze drums studied the alloy elements, composition, and structure morphology of copper drums by means of metallographic, scanning electron microscope (SEM) and determination of lead isotope abundances, and learned that most of the bronze drums contain copper, tin, lead, a small amount of arsenic, and a small amount of zinc, iron, antimony, and other elements (Lu et al., 2022). Because the properties of the drum materials are not only related to composition, temperature, morphology, and manufacturing process, but also related to the crystal structure of the substance that makes up the material. In order to have a more comprehensive and in-depth understanding of the composition of bronze drum materials, it is necessary to conduct qualitative and quantitative analysis by X-ray diffraction analysis of bronze drums. Unfortunately, the phase composition of bronze drums has not been reported so far. Figure 1 presents the site of the Majiang Bronze Drums from the popular regions of Hechi City, Guangxi, China. Here, we report the percentage content of the phase composition of the Majiang bronze drums obtained by metallographic method, SEM-EDS, and X-ray diffraction analysis.

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II. EXPERIMENTAL DETAILS

Six different Majiang-type bronze drums from Hechi City of Guangxi Province of China were provided by Guangxi Museum. The photos of two bronze drum No.0076 (diameter of 47.3 cm, height of 26.7 cm, and weight of 17.2 kg) and No.0093 (diameter of 48.1 cm, height of 27 cm, and weight of 16.8 kg) are shown in Figure 2a and 2b.

A small piece was cut from each bronze drum as a sample, which was separately prepared by traditional methods for

Figure 1. Site of the Majiang Bronze Drums from the popular regions of Hechi City, Guangxi, China. (▼).

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Figure 2. (a,b) Photographs of No.0076 and No.0093 bronze drums.

different instruments. Samples used for optical microscopy and SEM-energy dispersive X-ray spectroscopy (EDS, HItachi SN34000) were embedded in resin scaffolders and then polished by conventional methods and corroded by acid. The sample preparation for X-ray diffraction analysis is as follows: a small sample cut from a bronze drum is first filed into powder smaller than 10 μm using a steel file, and then the powder is loaded into an evacuated glass tube and annealed at 300°C for 5 days for stress relief and then slowly cooled to room temperature. The X-ray powder diffraction data of the samples from the bronze drums were obtained by using a Rigaku D/max 2500 V diffractometer with a $Cu_{K\alpha}$ radiation. The scan range was 15°–110° (2θ) with a step size of 0.02° and a count time of 2 s per step. The phase analysis of the samples and the initial lattice parameters determination for the alloy phases in the samples were carried out by using the Jade5.0 programs (Materials Data Inc., 1999). The X-ray diffraction technique was also employed to analyze the alloy phases in the samples of the bronze drums. Rietveld refinement was performed to determine the quantitative phase content.

III. RESULTS AND DISCUSSIONS

A. Metallographic analysis

The compositions of all the samples was determined by using SEM with EDS spectroscopy. All the bronze drums contain mainly Cu, Pb, Sn, and As. The metallographic photos of bronze drums No.0076 and No.0093 (×200) are shown in Figures 3a and 3b. The dark phase is Cu solid solution (Cu and As) or Cu, the white phase, corresponds to the component phase Cu_3Sn or $As_{0.2}Cu_{1.8}$ (in No.0093) and gray phase to $Cu_{10}Sn_3$, and the small white dots on the dark are Pb. The main elements and their compositions of the six bronze drums were obtained by using SEM with EDS spectroscopy (seen in Table 1).

B. Qualitative X-ray diffraction analysis

The X-ray diffraction qualitative analysis results showed that there are two groups of bronze drums with different X-ray diffraction patterns. One group consists of three bronze drums with drum codes No.0076, No.0068, and No.0083. Each bronze drum is composed of four phases (Cu, As) solid solution (Mertz and Mathewson, 1937), Pb (Bouad et al., 2003), Cu_3Sn (de Debiaggi et al., 2012), and $Cu_{10}Sn_3$ (Lenz and Schubert, 1971), seen in Figure 4. The other group also consists of three bronze drums with drum codes No.0093, No.0084, and No.0082. Each of these three samples of the bronze drums is composed of five phases Cu (de Debiaggi et al., 2011), Pb (Bouad et al., 2003), Cu_3Sn (de Debiaggi et al., 2012), $Cu_{10}Sn_3$ (Lenz and Schubert, 1971), and $As_{0.2}Cu_{1.8}$ (Schubert et al., 1957), seen in Figure 5.

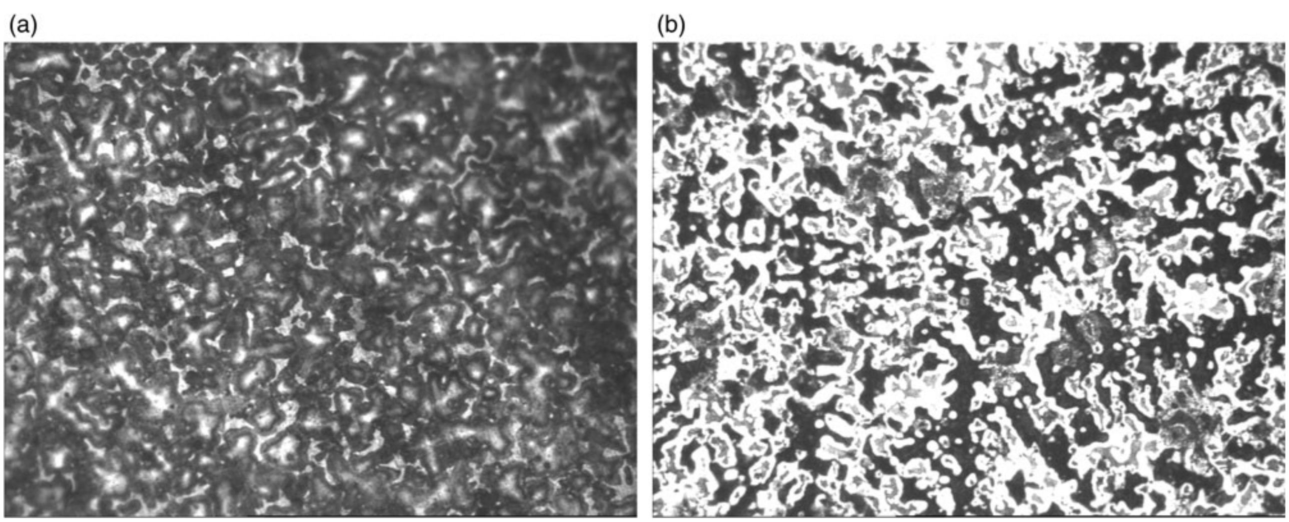

Figure 3. (a,b) Metallograph photos of the bronze drums No.0076 and No.0093 (×200).

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TABLE 1. The main elements and compositions of the Majing-type bronze drums in Guangxi Museum

No.	Drum code	Cu		Sn		Pb		As	
		Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%
1	0076	78.12	88.09	12.53	7.56	7.52	2.60	1.83	1.75
2	0068	78.14	87.25	15.97	9.55	3.93	1.35	1.96	1.86
3	0082	72.32	82.96	12.21	7.49	8.86	3.12	6.61	6.43
4	0083	75.72	86.94	8.53	5.24	12.10	4.26	3.65	3.56
5	0084	74.14	84.69	9.48	5.80	10.27	3.60	6.10	5.91
6	0093	75.30	83.56	12.74	7.57	3.96	1.35	8.00	7.52

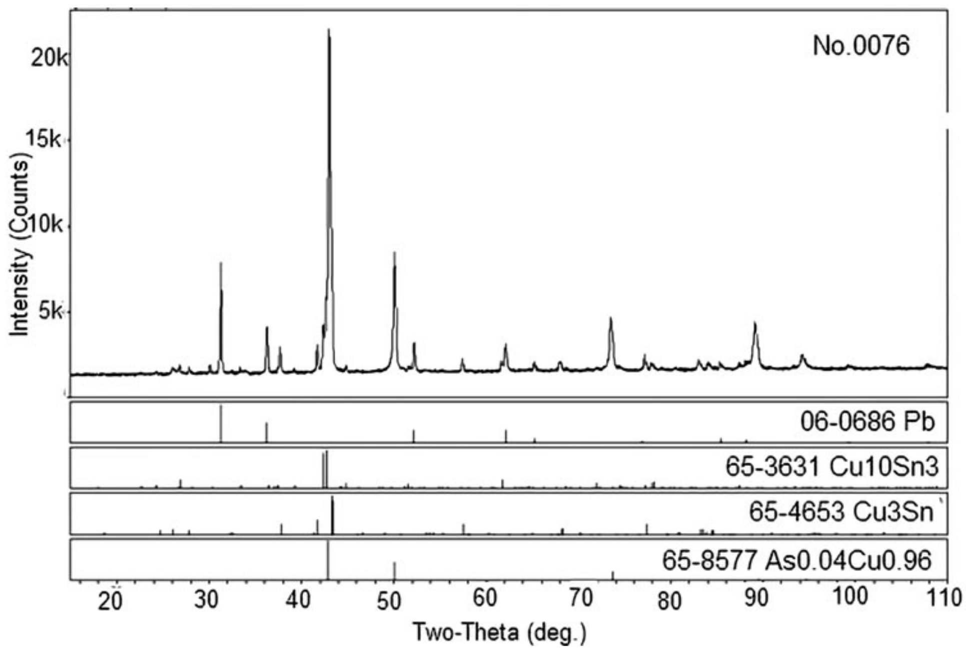

Figure 4. Results of qualitative phase analysis by X-ray diffraction for the No.0076 bronze drum.

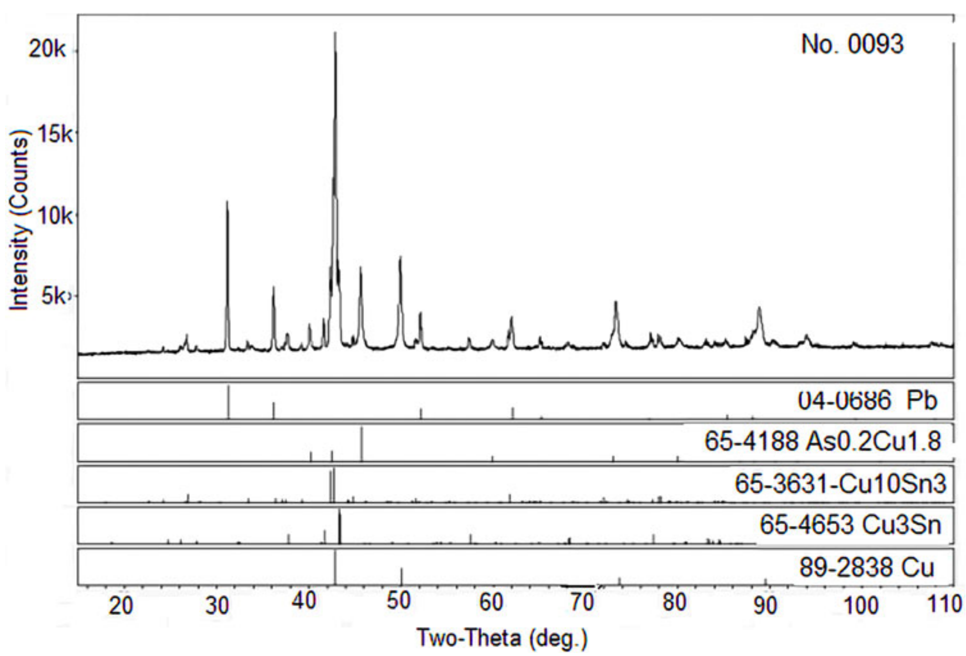

Figure 5. Results of qualitative phase analysis by X-ray diffraction for the No.0093 bronze drum.

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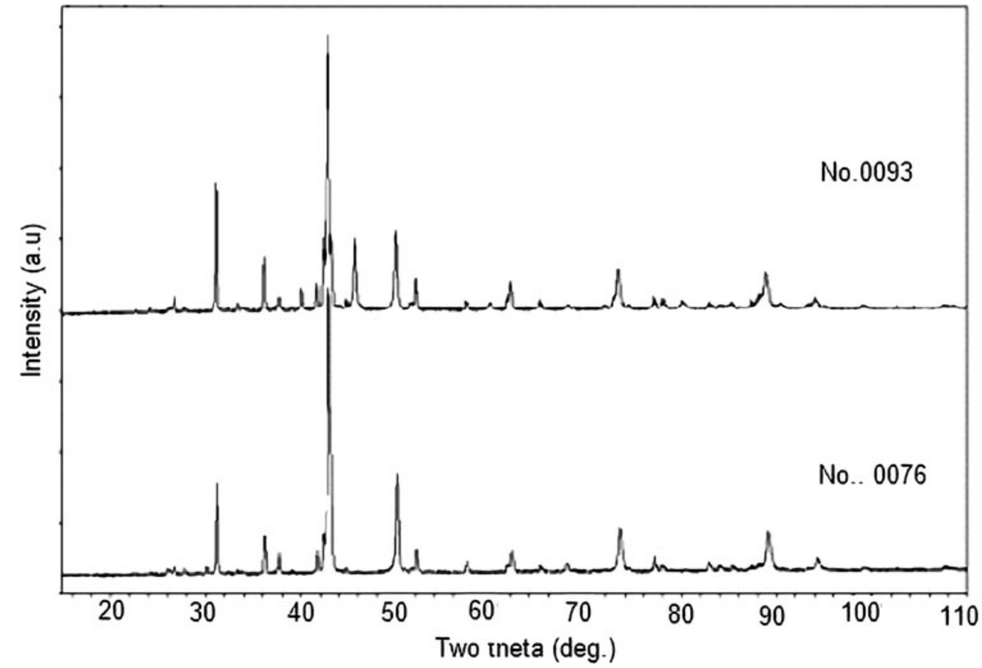

Figure 6. Comparison of X-ray diffraction patterns of No.0076 and No.0093 bronze drums.

Figure 6 shows the differences in the X-ray diffraction patterns of No. 0076 and No. 0093 bronze drums. In addition to many of the same X-ray diffraction lines, the No. 0093 bronze drum shows diffraction lines produced by the $As_{0.2}Cu_{1.8}$ phase, as seen in Figure 6.

C. Quantitative X-ray diffraction analysis

The Rietveld refinement was performed to do the quantitative phase analysis by using the DBWS9807 program (Young and Larson, 2000). The DMPLOT plot view program (Marciniak and Diduszko, 1997) was used to follow the refinement results. The pseudo-Voigt function was used for the simulation of the peak shapes. The lattice parameters obtained by the Jade5.0 program and the atomic parameters of the component phases, (Cu,As), Pb, Cu_3Sn, and $Cu_{10}Sn_3$ given in Table 3 were taken as starting values to do the quantitative phase analysis and refine the structural parameters of the four component phases existing in the No.0076 sample. A total of 56 parameters, including the lattice constants, full width at half maximum (FWHM), preferred orientation, atomic parameters, and thermal parameters were refined.

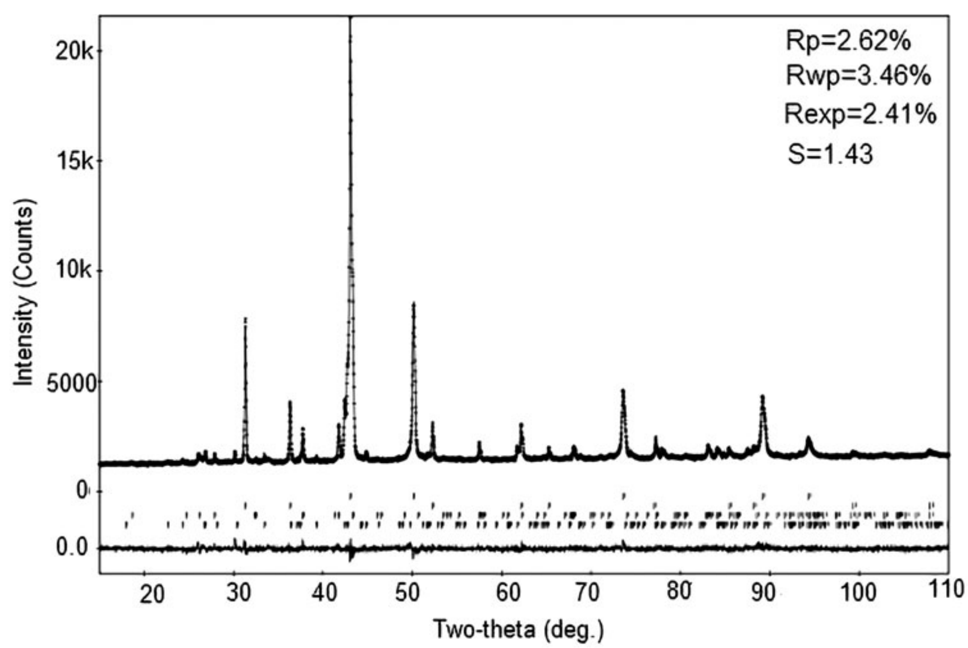

Figure 7. Rietveld refinement results for the No.0076 bronze drum. The crosses represent the observed data points, and the smooth line through them is the calculated pattern. The difference pattern (lower trace) is on the same scale as the measured pattern above. The row of tick marks indicates calculated reflection positions.

TABLE 2. The quantitative phase analysis results of the bronze drums

Drum code	Phases	Phase component (% Mass)	Composition (% Molar)
No.0076	$Cu_{0.96}As_{0.04}$	74.9 (4)	85.5(4)
	Pb	5 (1)	1.8(4)
	Cu_3Sn	10 (1)	10(1)
	$Cu_{10}Sn_3$	10 (1)	3.0(5)
	$R_p = 2.62\%$, $R_{wp} = 3.46\%$ and $R_{exp} = 2.41\%$, $s = 1.43$		
No.0093	Cu	54.4(5)	52.2(5)
	Pb	5.3(8)	1.5(2)
	Cu_3Sn	9(1)	7(1)
	$As_{0.2}Cu_{1.8}$	19(1)	36(3)
	$Cu_{10}Sn_3$	12(1)	3.0(4)
	$R_p = 2.85\%$, $R_{wp} = 3.87\%$, and $R_{exp} = 2.21\%$, $s = 1.74$		

The Reliability R-factors of Rietveld refinement are $R_p = 2.62\%$, $R_{wp} = 3.46\%$, and $R_{exp} = 2.41\%$, s = 1.43, respectively. The observed, calculated data and differences in the powder diffraction patterns of the sample of the bronze drum (No.0076) are shown in Figure 7. The Rietveld refinement results show that the bronze drum (No.0076) consists of $Cu_{0.96}As_{0.04}$, which possesses around 74.9 (4) (% Mass), and the other three phases, i.e., Cu_3Sn, $Cu_{10}Sn_3$, and Pb are 10(1), 10(1), and 5(1), respectively. Table 2 gives the quantitative phase analysis results and the crystal structure data (Table 3) of the component phases in the sample of bronze drum (No.0076).

The results of the quantitative phase analysis of No.0093 bronze drum, which contains five phases, namely Cu, Pb,

TABLE 3. The crystal structure data of the component phases for the bronze drums of No.0076 and No.0093

Drum code	Minerals	S. G.	Lattice parameters a (nm)	b (nm)	c (nm)	α (°)	β (°)	γ (°)	Ref.
No. 0076	$Cu_{0.96}As_{0.04}$	$Fm\bar{3}m$	0.364141 (2)	0.364141 (2)	0.364141 (2)	90	90	90	This work
			0.36405	0.36405	0.36405	90	90	90	Mertz and Mathewson (1937)
	Pb	$Fm\bar{3}m$	0.495329 (2)	0.495329 (2)	0.495329 (2)	90	90	90	This work
			0.4950 (1)	0.4950 (1)	0.4950 (1)	90	90	90	Bouad et al. (2003)
	Cu_3Sn	Pmmn	0.55158 (2)	0.433044 (8)	0.47671 (2)	90	90	90	This work
			0.5559	0.4329	0.4887	90	90	90	de Debiaggi et al. (2012)
	$Cu_{10}Sn_3$	$P6_3/m$	0.733713 (9)	0.733713 (9)	0.78636 (2)	90	90	120	This work
			0.7313	0.7313	0.787	90	90	120	Lenz and Schubert (1971)
No. 0093	Cu	$Fm\bar{3}m$	0.364759 (4)	0.364759 (4)	0.364759 (4)	90	90	90	This work
			0.3636	0.3636	0.3636	90	90	90	de Debiaggi et al. (2011)
	Pb	$Fm\bar{3}m$	0.495751 (8)	0.495751 (8)	0.495751 (8)	90	90	90	This work
			0.4950 (1)	0.4950 (1)	0.4950 (1)	90	90	90	Bouad et al. (2003)
	Cu_3Sn	Pmmn	0.55140 (2)	0.43337 (1)	0.47549 (2)	90	90	90	This work
			0.5559	0.4329	0.4887	90	90	90	de Debiaggi et al. (2012)
	$As_{0.2}Cu_{1.8}$	$P6_3/mmc$	0.259339 (1)	0.259339 (1)	0.424132 (3)	90	90	120	This work
			0.259	0.259	0.424	90	90	120	Schubert et al. (1957)
	$Cu_{10}Sn_3$	$P6_3/m$	0.73327 (1)	0.73327 (1)	0.78622 (2)	90	90	120	This work
			0.7313	0.7313	0.787	90	90	120	Lenz and Schubert (1971)

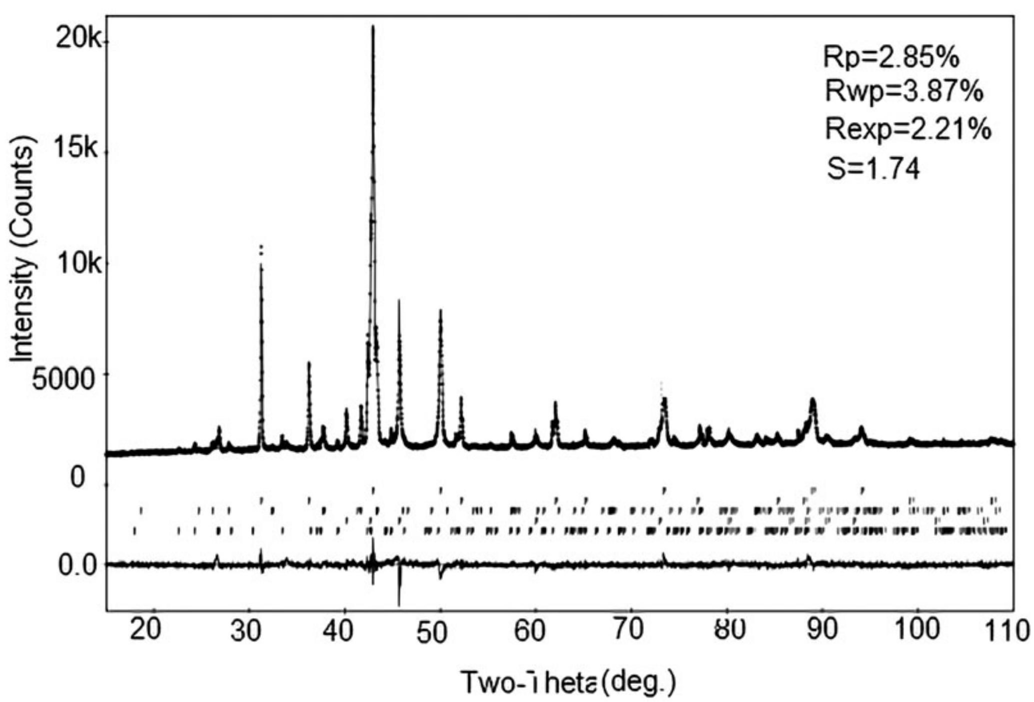

Figure 8. Rietveld refinement results for the No.0093 bronze drum.

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TABLE 4. Atomic coordinates for $Cu_{0.96}As_{0.04}$ (S.G. $Fm\bar{3}m$)

Atom	Position	X	Y	Z	Occupancy
Cu	4a	0	0	0	0.96
As	4a	0	0	0	0.04

TABLE 5. Atomic coordinates for Pb or Cu (S.G. $Fm\bar{3}m$)

Atom	Position	X	Y	Z	Occupancy
Pb	4a	0	0	0	1

TABLE 6. Atomic coordinates for Cu_3Sn (S.G. Pmmn)

Atom	Position	X	Y	Z	Occupancy
Sn	2a	1/4	1/4	0.331(21)	1
Cu	2b	1/4	3/4	0.682(4)	1
Cu	4f	0.4844(3)	1/4	0.836(3)	1

Cu_3Sn, $As_{0.2}Cu_{1.8}$, and $Cu_{10}Sn_3$ (Tables 2 and 3) were obtained by the same method. The Reliability *R*-factors of Rietveld refinement for No.0093 are $R_p = 2.85\%$, $R_{wp} = 3.87\%$, and $R_{exp} = 2.21\%$, s = 1.74., respectively. The observed, calculated data and differences in the powder diffraction patterns of the bronze drum (No.0093) are shown in Figure 8. The Rietveld refinement results show that the five phases in the No.0093 bronze drum are 54.4(5) wt.% Cu, 5.3(8) wt.% Pb, 9(1) wt.% Cu_3Sn, 19(1) wt.% $As_{0.2}Cu_{1.8}$, and 12(1) wt.% $Cu_{10}Sn_3$, respectively. The refinement results show that No.0076 bronze drum and No.0093 bronze drum contain the same four phases Cu or (Cu, As), Pb, Cu_3Sn, and $Cu_{10}Sn_3$, the difference is the percentage content of these four phases. In addition, No.0093 has $As_{0.2}Cu_{1.8}$ phase, while No.0076 does not. These show that the elements in the six bronze drums are basically the same, the difference is likely due to the casting temperature and the casting process. Tables 4–8 give the atomic parameters of the component phases $Cu_{0.96}As_{0.04}$, Cu, Pb, Cu_3Sn, $As_{0.2}Cu_{1.8}$, and $Cu_{10}Sn_3$.

TABLE 7. Atomic coordinates for $As_{0.2}Cu_{1.8}$ (S.G. $P6_3/mmc$)

Atom	Position	X	Y	Z	Occupancy
Cu	2c	0.3333	0.6667	0.25	0.93
As	2c	0.3333	0.6667	0.25	0.07

TABLE 8. Atomic coordinates for $Cu_{10}Sn_3$ (S.G. $P6_3/m$)

Atom	Position	X	Y	Z	Occupancy
Cu	2b	0	0	0	1
Cu	2d	1/3	2/3	0.75	1
Cu	4f	1/3	2/3	0.090	1
Cu	12i	0.673(2)	0.026(2)	0.085(1)	1
Sn	6h	0.298(2)	0.978(2)	0.25	1

IV. DISCUSSION

According to the Cu–As binary phase diagram (Figure 9) (Okamoto, 1994) the solid solubility of arsenic in copper is about 6 at.%, and the atomic radius of arsenic (0.126 nm) is close to that of copper (0.128 nm), so it is reasonable to

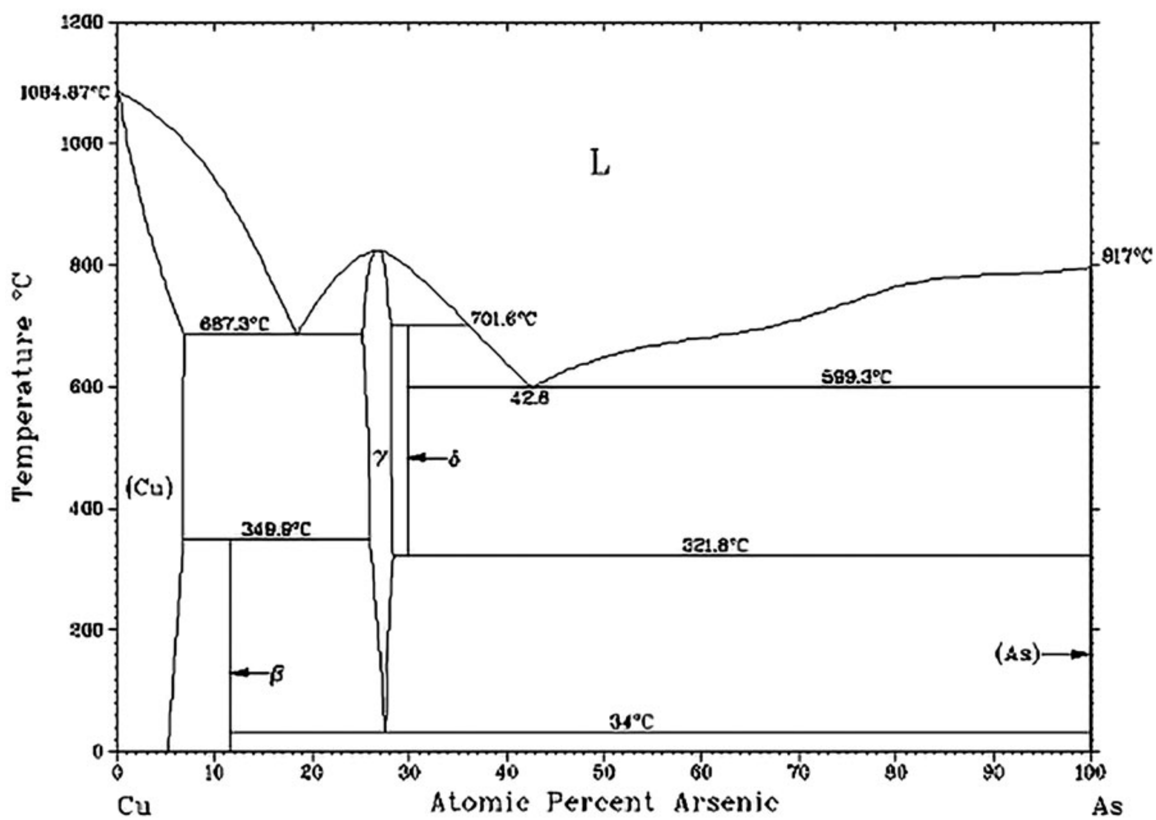

Figure 9. Cu–As binary phase diagram (Okamoto, 1994).

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have very small amounts of arsenic atoms in the position of copper unit cell to form a solid solution (Cu, As).

The phase content of the Pb phase of the bronze drums (No.0093) was 1.35 at.% obtained by SEM-EDS, this is quite close to the value of 1.5(2) at.% obtained by Rietveld refinement. The very small differences between the two results may be caused by different experimental instruments or experimental conditions.

V. CONCLUSION

Six samples were collected from six different Majing-type bronze drums from Hechi City of Guangxi Province of China in Guangxi Museum. The SEM,EDS results point out that the bronze drums contain mainly Cu, Pb, Sn, and As. The X-ray diffraction analysis and Rietveld refinement results point out that the sample of the bronze drum (No. 0076) contains four component phases of 74.9(4) wt.% $Cu_{0.96}As_{0.04}$, 5(1) wt.% Pb, 10(1) wt.% Cu_3Sn, and 10(1) wt.% $Cu_{10}Sn_3$ and the bronze drum (No. 0093) contains five component phases of 54.4(5) wt.% Cu, 5.3(8) wt.% Pb, 9(1) wt.% Cu_3Sn, 19(1) wt.% $As_{0.2}Cu_{1.8}$, and 12(1) wt.% $Cu_{10}Sn_3$, respectively.

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AUTHOR CONTRIBUTIONS

All authors contributed to the study conception and design. Chao Zeng: Sample preparation, data analysis, Rietveld refinement, and writing and revising. Wei He: Project administration, data analysis, writing, reviewing, and editing. Changzhong Liao: XRD data analysis, reviewing, and editing. All authors have read and agreed to the published version of the manuscript.

COMPETING INTERESTS

The authors have no financial or proprietary interests in any material discussed in this article.

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COMPLIANCE WITH ETHICAL STANDARDS

This article does not contain any studies with human participants or animals performed by any of the authors.

RESEARCH DATA POLICY AND DATA AVAILABILITY

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

AUTHOR CONTRIBUTIONS

All authors contributed to the study conception and design. Zeng Chao: Sample preparation, data analysis, Rietveld refinement, and writing and revising. He Wei: Project administration, data analysis, writing, reviewing and editing. Liao Changzhong: XRD data collection and analysis, editing. Chongjiang Li: Sample preparation and data collection. Wan Fubin: data analysis, reviewing and editing. All authors have read and agreed to the published version of the manuscript.

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