Crystal Structure and Electrical Resistivity of $ZrAg_{0.46}Al_{2.54}$

Wei HE*, Tonghan YANG, Hongrui LIU, Haichang ZHONG, Jingxian WEN
College of Materials Science and Engineering, Guangxi University, Nanning, Guangxi, 530004, P. R. China

ABSTRACT: The new $ZrAg_{0.46}Al_{2.54}$ ternary compound has been prepared by arc-melting and studied by means of X-ray powder diffraction technique. The structural refinement of $ZrAg_{0.46}Al_{2.54}$ was performed by using Rietveld method. The $ZrAg_{0.46}Al_{2.54}$ compound crystallizes in the cubic Cu_3Au-type structure with the space group $Pm\bar{3}m$ (No.221) and the lattice parameter of a = 4.1074 (1). The structural refinement of $ZrAg_{0.46}Al_{2.54}$ leads to the reliability R factors to be R_p = 0.05, R_{wp} = 0.065, R_{exp} =0.039 and S = 1.65, respectively. Electrical resistivity of $ZrAg_{0.46}Al_{2.54}$ was also measured between 5 and 300K. Temperature variation of the electrical resistivity of $ZrAg_{0.46}Al_{2.54}$ suggests its metallic character. The Debye temperature of $ZrAg_{0.46}Al_{2.54}$ is calculated to be Θ_D = 361K.
KEYWORDS: X-ray diffraction; Crystal structure; Electrical properties; Debye temperature;

1 INSTRUCTIONS

There is very limited investigation on the Al-Ag-Zr system reported in literature. There are ten intermediate phases in the Zr-Al system, i.e. Zr_3Al, Zr_2Al, Zr_5Al_3, Zr_3Al_2, Zr_4Al_3, Zr_5Al_4, ZrAl, Zr_2Al_3, $ZrAl_2$, and $ZrAl_3$, for which homogeneity ranges appear to be quite restricted [1]. The phase equilibrium of the Ag-Al system has been investigated and two compounds Ag_3Al and Ag_2Al were reported[2]. Two tetragonal intermediate phases with the approximate compositions AgZr and $AgZr_2$ were found in the Ag-Zr systems [3]. Much effort has been done in order to discover new ternary compounds with excellent properties. Fecht and his co-workers studied the sequence of phase transformations induced in the Zr-Al binary system by mechanical alloying of mixed Zr and Al powders [4]. In our recent study, new $ZrAg_{0.46}Al_{2.54}$ ternary compound has been found and its crystal structure has been determined by X-ray diffraction (XRD) technique. Electrical resistivity and the Debye temperature of $ZrAg_{0.46}Al_{2.54}$ have also been investigated. Here, we report the results.

2 EXPERIMENTAL DETAILS

The sample of $ZrAg_{0.46}Al_{2.54}$ with a total mass of 3 g, was prepared by arc-melting of initial pure materials (Zr: 99.9%, Ag: 99.999%, Al:99.99%) under high-purity argon atmosphere. The sample of $ZrAg_{0.46}Al_{2.54}$ was turned over and remelted three times to reach good homogeneity. The weight loss after melting was found to be less than 0.5%. The homogenizing annealing for $ZrAg_{0.46}Al_{2.54}$ was carried out at 900°C for 30 days in an evacuated quartz tube and cooled down to 500°C for 2 days, and then quenched into liquid nitrogen. The sample was ground in an agate mortar and pestle to a particle size of less than 10μm and annealed in an evacuated small quartz tube at 500°C for 5 hours, then quenched into liquid nitrogen.

Powder XRD data of $ZrAg_{0.46}Al_{2.54}$ were obtained from a Rigaku D/max 2500V diffractometer with a CuK_α (λ=1.54060Å). The (2θ) scan range was set from 10° to 110° with a step size of 0.02°. The index of the powder XRD data of $ZrAg_{0.46}Al_{2.54}$ was carried out by using a Jade5.0 program [5]. Electrical resistivity measurements for $ZrAg_{0.46}Al_{2.54}$ were performed in the temperature range of 5-300K by a conventional four-probe method with a voltage resolution of 10^{-7} V.

3 RESULTS AND DISCUSSION

3.1 *Crystal structure*

The XRD analysis proved the existence of the $ZrAg_{0.46}Al_{2.54}$ compound. All of the XRD patterns for $ZrAg_{0.46}Al_{2.54}$ were indexed successfully on a cubic structure with a reliability factor F_N to be F_{30} =

176.1(12) for the index [6]. The reflection conditions yield three possible space groups: $Pm\bar{3}m$ (No. 221), $P43$ (No. 207) and $P\bar{4}3m$ (No. 215) for the structure of $ZrAg_{0.46}Al_{2.54}$. Each unit cell contains one formula (4 atoms) based on the lattice parameters and the density (D_m = 5.00 g/cm^3). By careful comparison, it was found that $ZrAg_{0.46}Al_{2.54}$ is isostructural with the Cu_3Au with space group $Pm\bar{3}m$ (No.221) [7], which has the highest symmetry among the three possible space groups. Thus the space group $Pm\bar{3}m$ (No.221) was assigned to $ZrAg_{0.46}Al_{2.54}$. The structure of $ZrAg_{0.46}Al_{2.54}$ was refined by using Rietveld method with the DBWS9411 program [8]. The pseudo-Voigt function was used for the simulation of the peak shapes. The lattice parameters of $ZrAg_{0.46}Al_{2.54}$ obtained by the Jade 5.0 program and the atomic parameters of Cu_3Au [7] were input as the initial values to refine the structural parameters of $ZrAg_{0.46}Al_{2.54}$. A total of 14 parameters, including the lattice constants, full width at half maximum (FWHM), preferred orientation, atomic parameters and thermal parameters were refined. The structural refinement of $ZrAg_{0.46}Al_{2.54}$ leads to the reliability R factors to be R_p = 0.05, R_{wp} = 0.065, R_{exp} =0.039 and S = 1.65, respectively. The reliability R factor expressions for the Rietveld structural refinement are given below.

$$F_N = \frac{1}{\langle 2\theta \rangle}\frac{N_{obs}}{N_{cal}} \quad (1)$$

$$R_P = \frac{\sum |Y_i(obs) - Y_i(calc)|}{\sum Y_i(obs)} \quad (2)$$

$$R_{WP} = \left\{ \frac{\sum \omega_i (Y_i(obs) - Y_i(calc))^2}{\sum \omega_i (Y_i(obs))^2} \right\}^{1/2} \quad (3)$$

$$R_{EXP} = \left[\frac{N - P}{\sum_i^N \omega_i (Y_i(obs))^2} \right]^{1/2} \quad (4)$$

$$S = R_{WP} / R_P \quad (5)$$

The Rietveld refinement result points to that the $ZrAg_{0.46}Al_{2.54}$ compound adopts the structure of Cu_3Au. The Rietveld refinement result and crystal data for the $ZrAg_{0.46}Al_{2.54}$ compound are presented in Table 1. In the cubic structure of $ZrAg_{0.46}Al_{2.54}$, the Zr atoms are at the 1a positions, while the Ag and Al atoms occupy in the 3c positions (84.5 at.% Al + 15.5 at.% Ag). The refined atomic parameters for $ZrAg_{0.46}Al_{2.54}$ are given in Table 2. In the structure of $ZrAg_{0.46}Al_{2.54}$, the shortest distance of Zr-M (M=Ag, Al) is 2.9044 Å and is reasonable compared to the sum of Zr-M radii. There are 12 nearest atoms in the surrounding of the Zr and M atoms, respectively. The observed, calculated of XRD patterns of $ZrAg_{0.46}Al_{2.54}$ along with their residuals are shown in Fig.1.

3.2 *Electrical resistivity*

The electrical resistivity of $ZrAg_{0.46}Al_{2.54}$ was measured in the temperature range 5-300K with a voltage resolution of 10^{-7} V. The temperature dependence of the electrical resistivity for $ZrAg_{0.46}Al_{2.54}$ is prsented in Fig. 2. The electrical resistivity of $ZrAg_{0.46}Al_{2.54}$ is observed to fall from 0.1181 to 0.098 μΩ/cm between room temperature and 5K. In5-300K, the resistivity of $ZrAg_{0.46}Al_{2.54}$ decreases approximately linearly with the decrease of temperature pointing out its metallic-like behavior.

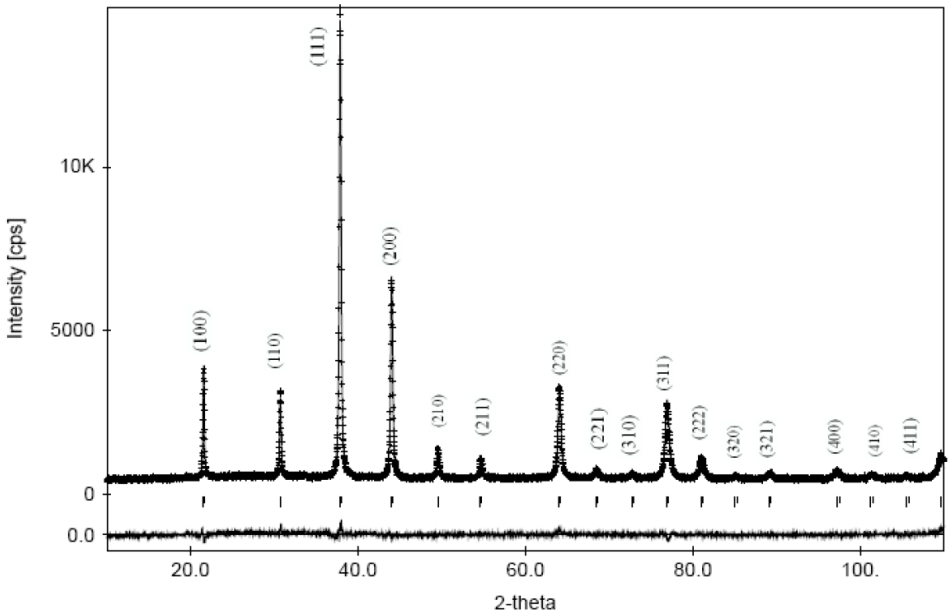

Fig. 1. Powder XRD patterns for $ZrAg_{0.46}Al_{2.54}$.

Table 1 Crystal data and lattice parameters for $ZrAg_{0.46}Al_{2.54}$

Formula	$ZrAg_{0.46}Al_{2.54}$
Space group	$Pm\bar{3}m$ (No.221)
a (Å)	a = 4.1074 (1)
Unit cell volume(Å^3)	69.295
Formula units per unit cell	1
Calculated density (g/cm^3)	5.030
F_N	F_{30} = 176.1(12)
R_p	0.05
R_{wp}	0.065
R_{exp}	0.039
S	1.65

Table 2. The atomic parameters for the $ZrAg_{0.46}Al_{2.54}$

Atoms	site	x	y	z	Occ.	B_{eq}(Å^2)
Zr	1a	0	0	0	1	0.459
M	3c	0	0.5	0.5	0.845 Al + 0.155 Ag	0.558

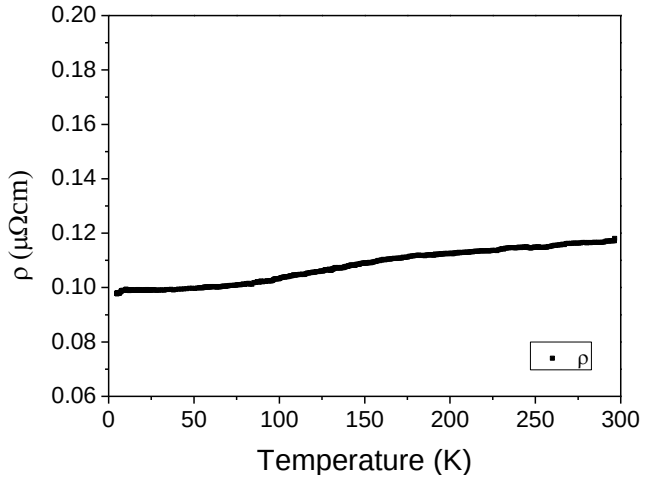

Fig. 2. Temperature dependence of the electrical resistivity for $ZrAg_{0.46}Al_{2.54}$.

3.3 *Debye Temperature*

As the characteristic temperature of vibration, the Debye temperature Θ_D is found to be closely related to the temperature factor of each component atom of a compound (here, B_{Zr}, B_{Ag} and B_{Al} for $ZrAg_{0.46}Al_{2.54}$). According to the Debye approximation[9 – 13], the following relationship can be obtained:

$$\frac{1}{4}\left(m_{Zr}B_{Zr}+3\times\left(0.843m_{Al}B_{Al}+0.157m_{Ag}B_{Ag}\right)\right) = \frac{6h^2T}{k\Theta_D^2}\left\{\Phi(x)+\frac{x}{4}\right\} \quad (6)$$

where $x=\Theta_D/T$, h is Planck's constant, k is Boltzmann's constant, T is the experimental temperature, and $\Phi(x)$ is the Debye integral function, which can be calculated from:

$$\Phi(x)=\frac{1}{x}\int_0^x \frac{y}{e^y-1}dy \quad (7)$$

Further define:

$$G=\frac{kT}{24h^2}\left(m_{Zr}B_{Zr}+3\times\left(0.843m_{Al}B_{Al}+0.157m_{Ag}B_{Ag}\right)\right) \quad (8)$$

Than Eq. (1) can be rewritten as

$$\Phi(x)+\frac{x}{4}=Gx^2 \quad (9)$$

The value of G can be calculated from Eq. (8) to be G = 0.712 for $ZrAg_{0.46}Al_{2.54}$. By plotting the two curves which represent $y_1=\Phi(x)+x/4$ and $y_2=Gx^2$, as shown in Fig. 3, the value of x = 1.2055 was obtained from the point where the two curves meet. Then the Debye temperature of $ZrAg_{0.46}Al_{2.54}$ can easily be calculated to be $\Theta_D = T_x$ = 361K.

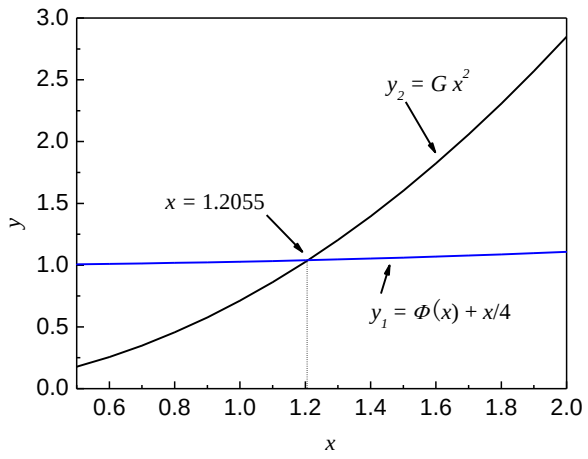

Fig. 3. Calculation of Θ_D by Debye approximation.

4 CONCLUSION

The crystal structure of the new $ZrAg_{0.46}Al_{2.54}$ ternary compound was determined by XRD technique and its structure was successfully refined by using Rietveld method. The $ZrAg_{0.46}Al_{2.54}$ compound crystallizes in an cubic Cu_3Au-type structure, space group $Pm\bar{3}m$ (No.221) with a = 4.1074 (1) Å. The reliability factor, F_N, for the index of $ZrAg_{0.46}Al_{2.54}$ is F_{30} = 176.1(12). The reliability R-factors of Rietveld refinement are R_p = 0.05, R_{wp} = 0.065 and R_{exp} = 0.039, respectively. Measurement of the electrical resistivity of $ZrAg_{0.46}Al_{2.54}$ from 5-300K suggests its metallic character. The Debye temperature of $ZrAg_{0.46}Al_{2.54}$ is calculated to Θ_D = 361K from the temperature factors of Rietveld refinement.

5 ACKNOWLEDGEMENTS

The authors would like to express their gratitude to Professor Cheng Dong (Institute of Physics, Chinese Academy of Sciences) for his assistance in electrical measurements. This work was jointly supported by the National Natural Science Foundation of China (Nos. 51261002 & 51461004), the Guangxi Natural Science Foundation (No. 2012GXNSFAA053211) and International Centre for Diffraction Data Grant-in-Aid program (No. 08-03).

REFERENCES

[1] Peruzzi A and Abriata J.P. Al-Zr (Aluminum-Zirconium), in Binary Alloy Phase Diagrams, ASM International, The Materials Information Society, Materials Park, OH, (1992), p. 241.

[2] McAlister AJ. Ag-Al (Silver-Aluminum), in Binary Alloy Phase Diagrams, ASM International, The Materials Information Society, Materials Park, OH, (1992), p. 8

[3] Karakaya I. and Thompson W.T. Ag-Zr (Silver-Zirconium), in Binary Alloy Phase Diagrams, ASM International, The Materials Information Society, Materials Park, OH, (1992), p. 117

[4] Fecht HJ, Han G, Fu Z, Johnson WL, J. Appl. Phys. 1990; 67:1744

[5] Jade5.0, XRD pattern processing Materials, Data Inc. 1999.

[6] Smith GS, Snyder PL. J. Appl. Cryst., 1979; 12: 60-62.

[7] Pearson's Handbook, Crystallographic Data for Intermetallic Phases, Desk edition, P. Villars, ASM International, The Materials Information Society, Materials Park, OH, 1997

[8] Young AR, Larson AC, PaivaSantos CO. User's guide to program DBWS9807a for RIETVELD ANALYSIS OF XRAY AND NEUTRON POWDER DIFFRACTION PATTERNS**.** R. School of Physics, Georgia Institute of Technology. Atlanta, Georgia, Copyright 1998, 1999.

[9] Willins BTM, Pryor AW. Thermal Vibrations in Crystallorgraphy, Cambridge University Press, London, 1979

[10] Lu SS, Liang JK. Acta Phys. Sin. 1981; 30:1361-1364 (in Chinese).

[11] Lu SS, Liang JK, Acta Phys. Sin. 1981; 30:1498-1502 (in Chinese).

[12] Chen XL, Liang JK. Mod. Phys. Lett. B 1999; 13:285-290.

[13] Wei ZF, Chen XL. Chin. Phys. Lett. 2002; 19 (2): 249-251.