On the Crystal Structure of $HgZn_3$

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The crystal structure of the intermetallic phase $HgZn_3$ was determined using X-ray single crystal and powder diffraction methods. The phase belongs to the orthorhombic system, most probable space group being $Cmc2_1$, and appears to be isostructural with β'-Cu_3Ti. Under standard preparative conditions a statistical distribution of both atomic species was observed.

Introduction

The existing literature data on the system Hg–Zn are relatively old. Moreover, a number of investigations was carried out using micrography, dilatometry and electrical conductivity. Far less experimental material was gathered on the basis of x-ray diffraction procedures. Due to the above-mentioned reasons the system may be considered as ill-defined in terms of the crystal structure of identified phases. According to early authors [1, 2] there are three phases in the system *i.e.* narrow primary solid solution of mercury in zinc (0.5–1.5 a/o, α-phase); a β-phase is stable below 253 K and within the composition range 55–68 a/o Zn with no data about its crystal structure, a γ-phase is stable below 323 K within the compositions 70–77 a/o Zn and a narrowing phase field as the temperature decreases. For this latter phase Simson [1] gave hexagonal lattice parameters $a = 270$ pm and $c = 540$ pm. The hexagonal cell was later confirmed by Løvold-Olsen [2] with new and probably more precise lattice constants: $a = 271.3$ pm, $c = 540.8$ pm. Due to the rather broad homogeniety region the stoichiometries were given as $HgZn_3$ or Hg_3Zn_8. Finally, there are no data on the solid solubility of mercury in zinc.

The object of this work was to study more thoroughly the crystal structure of γ-phase because of a rather puzzling axial ratio ($c/a \doteq 2$) and the frequent appearance of some additional faint diffraction maxima in aged samples.

Results and Discussion

X-ray powder patterns of the γ-phase having the exact stoichiometric composition $HgZn_3$ could be indexed on the basis of several different unit cells. Even though the one proposed by Løvold seems to be acceptable we tried to obtain single crystal fragments in order to define the crystal structure more precisely.

By combining the x-ray powder diffraction data and Weissenberg photographs the unit cell of $HgZn_3$ may now be described as having orthorhombic symmetry with the following lattice constants: $a = 270.8 \pm 0.1$ pm, $b = 469.6 \pm 0.2$ pm, $c = 547.1 \pm 0.2$ pm. The above values were obtained with the use of Visser's automatic indexing program, only the choice of axes is ours for the reasons to be explained below.

The following systematic extinctions were observed:

$0\,0\,l$	$l = 2n$
$0\,k\,0$	$k = 2n$
$h\,0\,0$	$h = 2n$
$0\,k\,l$	$k = 2n$
$h\,0\,l$	$h + l = 2n,\ h = 2n,\ l = 2n$
$h\,k\,0$	$h + k = 2n$
$h\,k\,l$	$h + k = 2n$

The literature search for eventually existing isostructural phases focused our attention to the high-temperature polymorph of Cu_3Ti (β'-Cu_3Ti). It was found, indeed, that the x-ray powder diffraction patterns are similar which is not surprising because the stoichiometry is identical and the relative order of atomic numbers is the same. In clear analogy

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with the above mentioned example and the fact that for amalgams such as Hg–Zn, the temperatures of preparation and storage should be considered as high, we propose the designation γ'-$HgZn_3$. The relevant x-ray diffraction data are given in Table I.

Table I. Diffractometer data for $HgZn_3$
(Cu target, Ni filter).

$h\ k\ l$	d_o	d_c	I_o	I_c
0 0 2	2.7352	2.7357	54	52
0 2 0	2.3476	2.3478	28	28
1 1 0		2.3456		
0 2 1	2.1570	2.1575	100	111
1 1 1		2.1559		
0 2 2	1.7822	1.7816	24	23
1 1 2		1.7807		
0 2 3	1.4400	1.4403	27	29
1 1 3		1.4398		
0 0 4	1.3690	1.3678	3	6
1 3 0	1.3562	1.3551	12	9
2 0 0	1.3531	1.3538	5	5
1 3 2	1.2163	1.2143	12	13
2 0 2	1.2130	1.2133	6	8
0 2 4	1.1824	1.1819	1	1
0 4 0	1.1748	1.1738	3	3
2 2 0	1.1722	1.1728	1	1
0 4 1	1.1485	1.1478	7	2
2 2 1	1.1459	1.1467	5	12
0 4 2	1.0797	1.0788	2	4

Pycnometrically determined density (decalin) of $HgZn_3$ is 9.28 gcm^{-3} corresponding to 3.92 atoms per unit cell *i.e.* one formula unit. Since the experimentaly determined systematic extinctions match those for β'-Cu_3Ti the following atomic positions in the space group $Cmc2_1$ (C_{2v}^{12}) were assumed:

$$0,\ y,\ z;$$
$$0,\ \bar{y},\ 1/2 + z$$
$$1/2,\ 1/2 + y,\ z$$
$$1/2,\ 1/2 - y,\ 1/2 + z$$

The calculation of x-ray diffraction intensities was carried out for statistical distribution. The best agreement between calculated and observed intensity values obtained for $z = 0.250$ and $y = 0.357$ (See Table I), are considered good enough to prove the assumed atomic positions *i.e.* isostructural relationship with β'-Cu_3Ti. It is worth mentioninig that a number of other intermetallic phases of the general composition 3:1 belong to the same structure type, the most notable examples being Ag_3Sb [4, 5], Ag_3Sn [6] and Ni_3Sn [7]. In all these phases, except Cu_3Ti the stoichiometry may deviate from ideal 3:1 ratio explaining thus the ambiguity $HgZn_3$–Hg_3Zn_8.

This crystal structure should be viewed as a distorted variant of hexagonal close packing. The radius ratio for these phases ranges from 0.77 (Ni_3Sn) and 0.90 (Ag_3Sb), with $r_{Zn}/r_{Hg} = 0.89$, fitting in between. Packing density is slightly reduced (approximatelly 5%). Interatomic distances in $HgZn_3$ with coordination number 12, being split as $2+2+4+4$, are 270.8 and 321.3 pm.

In some of the afore-mentioned intermetallics the appropriate thermal treatment produces ordering. As a rule such process leads to the doubling of the cell volume through the doubling of *a* axis. This phenomenon has been quantitatively elaborated for Cu_3Ti. The crystal structure of the ordered phase belongs to the space group Pmmn with copper atoms in positions 4f) and 2b), and titanium atoms occupying positions 2a). It is interesting to note that Ni_3Ta exists in the ordered form only [3]. The phase Ag_3Sb which at higher temperatures has a statistical atomic arrangement and was originally erroneously indexed as hexagonal on the basis of x-ray powder diffraction data, undergoes at lower temperatures a transition to the ordered state with the accompanying transformation of the unit cell *i.e.* into one with a double value of *a* axis [8].

In order to detect the eventual ordering in $HgZn_3$, samples were left at room temperature and at 253 K for several months. No changes in the diffraction patterns were observed for the former set of samples but in the latter faint extra diffraction maxima have appeared. Due to the extremely sluggish processes at such low temperatures no claims could be made as to the nature and significance of this observations but further studies regarding this problems are underway.

Experimental

Alloy samples were prepared by direct synthesis from extrapure mercury ("Kemika", Zagreb) pretreated with concentrated nitric acid, thoroughly washed with redistilled water and dried with aceton, and electrolytic zinc ("Laphoma"-Skopje > 99.9%). Components were sealed off in evacuated quartz vials, put in a tightly closed heavy steel container heated up to 700 K and then either slowly cooled down to the room temperature (20 K/hour) or rapidly quenched in the stream of running water. No difference in X-ray powder diffraction patterns of both set of samples was observed. The procedure which enabled us to obtain several single crystal fragments of $HgZn_3$ was as follows: Samples were subjected to a homogenization treatment at 573 K in vacuo, cooled, carefully crushed in an agate mortar and again kept in evacuated glass vials at the same temperature for another 3 days. From such samples few single crystal fragments were isolated.

X-ray powder diffraction patterns were taken at General Electric Diffractometer XRD-6; copper radiation and Ni-filter being used throughout the work. Single crystal photographs were obtained using standard Weissenberg method on a Philips 1040 unit employing also Ni filtered Cu radiation. Indexing and lattice parameters calculation were performed using Visser's program. Much of the intensity calculations were done with the help of LAZY PULVERIX program.

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