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# THE BEHAVIOUR OF THE LATTICE PARAMETERS IN THE Bi-Sn-Zn SYSTEM

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#### Abstract

Lattice parameters, coefficients of thermal expansion and mass density were determined by means of X-ray powder diffraction between 30 and 180 °C (or 240 °C - depending on samples' composition). Rietveld refinement was performed in order to obtain phases' lattice parameters at each temperature. The Panalytical X'Pert Pro MPD was used for room temperature X-ray diffraction experiments (RT-XRD) with bulk samples. The aim was to identify the phases that were present in the sample, as well as, their lattice parameters. For some samples, powder high temperature X-ray diffraction measurements (HT-XRD) were also performed, under a vacuum of  $10^{-5}$  mbar or an argon atmosphere.

It was found that the lattice parameters of (Bi), (Sn) and (Zn) don't change with the composition, at room temperature, as expected since all samples belong to the three phase region. It was also concluded that (Bi) behaves like an isometric crystalline solid on the contrary of (Zn) that has different expansion coefficients for different crystallographic directions a (= b) and c.

Keywords: Bi-Sn-Zn, (RT/HT)-XRD, lattice parameters, expansion coefficients, mass density.

## 1. Introduction

Health problems (especially neurological and birth malformations) may arise from the excess of lead in human bodies. The excess of lead is due to water contamination. Hence, lead was added to the list of apprehensions with the environment [1].

The objective of COST 531 action "Leadfree Solder Materials" [2] (European

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Cooperation in the field of Scientific and Technical Research) was the study of systems that may be used as lead-free solders. The selection of these systems was based on technical and health hazard considerations. The crucial technological properties to be analyzed should be: melting temperature, wettability, surface tension, viscosity of the liquid alloys at different temperatures, oxidation behaviour, thermomechanical fatigue, etc.

The evaluation of experimental phase diagrams, measurement of the thermodynamic properties and consequent optimisation of the corresponding phase diagrams (using CALPHAD method) were some of the aims of the COST 531 action.

Bi-Sn-Zn was one of the systems studied in the scope of the above mentioned program.

The coefficient of thermal expansion and mass density are properties that were object of measurements since their knowledge is essential when solders are the issue.

This study complements other previous studies done for the system Bi-Sn-Zn [3, 4].

## 2. Experimental

Nine samples corresponding to vertical sections with w(Sn)  $\sim$  5 %, 40 % and 59 % were chosen for this study (Fig. 1). They had  $\sim 20$  mm in diameter,  $\sim 3$  mm in high and  $\sim$ 2 g in weight. Samples were prepared by mixing pure Bi (> 99.8 %), Sn (> 99.5 %) and Zn (> 99.9 %). The samples were then putted in alumina crucibles and melted in a resistance furnace under an argon atmosphere. The nominal compositions of the samples were confirmed by X-ray Fluorescence (XRF) and Atomic Absorption Spectroscopy (AAS). All samples were homogenized at 120 °C for 60 minutes and



Fig. 1. Compositions of the prepared samples (signed by double triangles) over the calculated phase diagram using the Gibbs equations from [4], a) at 298 K and b) at 393 K.

slowly cooled down to the room temperature in a rate less than 2 °C/min.

Bulk RT-XRD measurements were performed to identify the present phases. For some samples, powder HT-XRD measurements were also performed, under a vacuum of 10<sup>-5</sup> mbar or an argon atmosphere. The furnace used is an Anton Parr Chamber applied to the Panalytical X'Pert Pro MPD. CuK $\alpha$  or primary monochromated CuK $\alpha_1$  radiations were used. Patterns were collected from 5 to 120° (2 $\theta$ ) with steps of 0.01° and counting time of 10 s.

### 3. Results

## 3.1. Room Temperature

RT-XRD data were refined using Rietveld method [5] applied on the Fullprof software [6]. The  $R_p$ ,  $R_{wp}$  and  $R_B(Bi)$ ,  $R_B(Sn)$  and  $R_B(Zn)$  are of the order of  $R_p = 13$  %,  $R_{wp} = 14$  %,  $R_B(Bi) = 2$  %,  $R_B(Sn) = 1$  % and  $R_B(Zn) = 1$  %. (Bi) was refined as rhombohedral (A7), R-3m, (Sn) was refined as tetragonal (A5), I 4<sub>1</sub>/amd (bct) and (Zn) was refined as hexagonal (A3), P 6<sub>3</sub>/mmc (hcp). Results for two of the nine samples measured, with compositions w(Bi) = 23.7

%, w(Sn) = 38.5 %, w(Zn) = 37.8 % and w(Bi) = 53.3 %, w(Sn) = 4.9 %, w(Zn) = 41.8 % can be observed in Figs. 2 and 3, respectively.

By the observation of the phase diagram at room temperature (298 K) and at 393 K (Fig. 1), it can be seen that the only phases that show the possibility of having slightly different lattice parameters than the respective pure element, are (Sn) and (Bi). When comparing our Rietveld refinements data with Sn and Bi pure elements data [7], it can be observed that (Sn) and (Bi) are the phases that present some discrepancy (for (Sn) especially for a = b and for (Bi) especially for c) (if [7] is considered), as expected from the phase diagram.

For (Sn), the difference between the average a = b lattice parameter for (Sn) and for pure Sn is 0.162 % of the value of Sn pure and the difference between the average c lattice parameter for (Sn) and the value for Sn pure is 0.088 % of the value for Sn pure



Fig. 2. RT-XRD pattern for a sample with composition w(Bi) = 23.7 %, w(Sn) = 38.5 % and w(Zn) = 37.8 % after Rietveld refinement



*Fig. 3. RT-XRD* pattern for a sample with composition w(Bi) = 53.3 %, w(Sn) = 4.9 % and w(Zn) = 41.8 % after Rietveld refinement

(Fig. 4) considering [7].

For (Zn), the difference between the average a = b lattice parameter for (Zn) and the value for Zn pure is 0.038 % of the value for Zn pure and the difference between the average c lattice parameter for (Zn) and the value for Zn pure is 0.061 % of the value for

Sn pure (Fig. 5) considering [7].

For (Bi), the difference between the average a = b lattice parameter for (Bi) and the value for Bi pure is 0.095 % of the value for Bi pure and the difference between the average c lattice parameter for (Bi) and the value for Bi pure is 0.238 % of the value for



Fig. 4. Lattice parameters for (Sn) found after Rietveld refinement. a) a = b (Å) b) c (Å). Inside the circle the value for pure Sn from [7] and inside the square the value for pure Sn from [8].



Fig. 5. Lattice parameters for (Zn) found after Rietveld refinement. a) a = b (Å) b) c (Å). Inside the circle the value for pure Zn from [7] and inside the square the value for pure Zn from [9].

Bi pure (Fig. 6) considering [7].

As expected the difference between the measured values of the lattice parameters for (Zn) and Zn [7,9] are of the order of the experimental error (Fig. 5). The major differences between the lattice parameter of the pure element and of the respective phase are for a = b in the case of (Sn) and for c in the case of (Bi). For both cases the value of

the experimental lattice parameters are higher than those for the pure elements if [7] is considered. That is expected in what concerns (Sn) since it dissolves Bi and Bi as a higher covalent radius than Sn. If Bi occupies Sn sites in the lattice it is expected that the resulting lattice will be expanded when compared with that from pure Sn. For the latter reason, what is not expected is that



Fig. 6. Lattice parameters for (Bi) found after Rietveld refinement. a) a = b (Å) b) c (Å). Inside the circle the value for pure Bi from [7] and inside the square the value for pure Bi from [10].

the lattice will be contracted (which is what happens in the case of (Bi) if we take [7] into account) when Sn substitutes Bi. Hence, it maybe supposed that the discrepancy found for (Bi), when compared with Bi from [7], is maybe due to two possibilities: the presence of Sn atoms in interstitial spaces (in the c direction) or to experimental inaccuracies. If we take the values for pure Bi from [10], we can consider that the substitution of Bi by Sn results in a contraction of the lattice in the a = b direction.

## 3.2. High Temperature

If a crystalline solid is isometric (has the same structural configuration throughout), the expansion will be uniform in all dimensions of the crystal. If it is not isometric, there will be different expansion coefficients for different crystallographic directions, and the crystal will change shape as the temperature changes.

The linear expansion coefficient, , is given by equation 1:

$$\alpha_L = \frac{1}{L(T=0^{\circ}C)} \frac{dL}{dT} \tag{1}$$

L is one of the dimensions of the solid. In this case we've made L has a lattice parameter: a = b or c. dL/dT is the obtained by linear regression of the data obtained experimentally.

If a crystalline solid is isometric, the linear expansion coefficient . (Bi) seems to be isometric  $\alpha_{a=b} \cong c$  (Fig. 7 a) and b)) but not (Zn) (Fig. 8 a) and b)). For polycrystalline Zn  $\alpha_L = 3.97E \cdot 5K^{-1}$  (for 20°  $\leq T \leq 250$  °C) as it is tabulated in [11]. For a single crystal  $\alpha_c = 6.1E \cdot 5K^{-1}$  (for 0°  $\leq T \leq 100$  °C) and  $\alpha_{a=b} = 1.5E \cdot 5K^{-1}$  (for 0°  $\leq$ 



Fig. 7. (Bi) lattice parameters as a function of temperature a)  $a = b(T) \ b) \ c(T)$  obtained with a sample with  $w(Bi) = 68.4 \ \%$ ,  $w(Sn) = 6.0 \ \%$  and  $w(Zn) = 25.6 \ \%$ . Experimental expansion coefficient in comparison with that from [13]. Points surrounded by a circle were not considered for the calculus

 $T \le 100$  °C) [11]. Our results (Fig. 8 a) and b)) are more in agreement with those for a single crystal, indicating thermal anisotropy.

(Zn) has a hexagonal structure in which d (interplanar distance) is related with h, k, l (the Miller indices) and with the lattice parameters a = b and c, as follows:

$$\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}$$
(2)

If a reflection corresponds to [002], h = 0, k = 0 and l = 2, equation 2 becomes:  $1/d = \pm \ell/c$ . In this case, it can be written: c = d/2. By analysing the reflection [002] (Fig. 9) we can have a direct measure of the c lattice parameter. We've compared c obtained by the analysis of [002] and by Rietveld refinement in Fig. 10. We've also compared obtained by both ways.

In Fig. 11 it can be observed the volume of the unit cell of (Zn) as a function of the temperature as well as the experimental expansion coefficient.

In Fig. 12 it was plotted the mass density as a function of temperature that was calculated using the equation:

$$\rho = \frac{nM}{V_{\text{unit cell}} N_A} \tag{3}$$

In which *n* is the number of atoms per unit cell, *M* the atomic weight, the volume of the unitary cell and  $N_A$  the Avogadro's number.

Using the equation that resulted from the linear fit (Fig. 12), we could calculate the mass density at 250°C as  $\rho_{250}o_C = 6.929$ gcm-3 and compare it with the experimental result from [12],  $\rho_{250}o_C = 6.674$  gcm<sup>-3</sup>, which corresponds to a difference of 3.8 % (in comparison with the value in [12]). It was also calculated the value at 750 °C, for Zn liquid,  $\rho_{750}o_C = 6.423$  gcm<sup>-3</sup> and compared with  $\rho_{750^{\circ}C} = 6.265 \text{ gcm}^{-3}$  from [12]. It corresponds to a difference of 2.5 % (in comparison with the value in [12]). For Zn liquid, the data from [12] was linear fitted and it was obtained:  $\rho(kgm^{-3}) = 6877$ - $0.8199 \cdot T(^{O}C)$  that is comparable with that from Fig. 12.

It was also possible to compare our result, at 20 °C,  $\rho_{20}o_C = 7.162 \text{ gcm}^{-3}$ , with that from [13]  $\rho_{20}o_C = 7.140 \text{ gcm}^{-3}$ , which corresponds to a difference of 0.3 % (in comparison with the value in [13]).



Fig. 8. (Zn) lattice parameters as a function of temperature a) a = b(T) b) c(T) obtained with a sample with w(Bi) = 68.4 %, w(Sn) = 6.0 % and w(Zn) = 25.6 %. Experimental expansion coefficient in comparison with that from [13]. Points surrounded by a circle were not considered for the calculus.



Fig. 9. Zoom of the HT-XRD diffraction patterns as a function of the temperature obtained for a sample with w(Bi) = 68.5 %, w(Sn) = 5.7 % and w(Zn) = 25.8 %. At T >120 °C, Sn peaks cannot be distinguished anymore. For (Zn) the reflection corresponding to [002] suffers a deflection with the increasing temperature



Fig. 11. (Zn) unit cell volume as a function of temperature obtained with a sample with w(Bi) = 68.4 %, w(Sn) = 6.0 % and w(Zn) = 25.6 after Rietveld refinement. Experimental calculated expansion coefficient.



Fig. 10. (Zn) c lattice parameter as a function of temperature obtained with a sample with w(Bi) = 68.4 %, w(Sn) = 6.0 % and w(Zn) = 25.6. c parameter was found after Rietveld refinement (squares) and after the analysis of the reflection corresponding to [002] (circles).



Fig. 12. (Zn) mass density as a function of temperature obtained with a sample with w(Bi) = 68.4 %, w(Sn) = 6.0 % and w(Zn) =25.6 after Rietveld refinement. Mass density of Zn at a temperature near room temperature [13]

## 4. Conclusions

Both results at room temperature and at high temperature are in good agreement with what was expected by the observation of the phase diagram and by analysis of the available references.

At room temperature, the dissolution of Bi in (Sn) will make the lattice expand. The interpretation of the dissolution of Sn in (Bi) depends on the values considered for Bi pure.

At high temperatures, (Bi) behaves as an isometric solid but (Zn) shows thermal anisotropy, since  $\alpha_c(Zn) > \alpha_{a=b}(Zn)$  as it is expected for a single crystal but not for a polycrystalline solid. Nevertheless, the calculated mass density is in agreement with the published data for room temperature, 250°C and 750 °C.

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