

ON THE SYNTHESIS OF Bi – BASED PRECURSORS FOR LEAD – FREE SOLDERS DEVELOPMENT

V. Gandova^{*}, K. Lilova^{*}, H. Malakova^{*}, B. Huber^{**}, N. Milcheva^{*},
H. Ipser^{**}, J. Vrestal^{***} and G. Vassilev^{*#}

^{*}University of Plovdiv, Faculty of Chemistry, 4000 Plovdiv, Bulgaria,

^{**}University of Vienna, Department of Inorganic Chemistry
Materials Chemistry, A-1090 Wien, Austria

^{***}Masaryk University, Faculty of Science, Brno, Czech Republic

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Abstract

Preliminary studies on the design of lead-free solders precursors by wet chemistry methods are presented. The main objective is to assess the impact of the way of hydroxide precipitates preparation on the metal elements content of the precipitates. Namely, ternary hydroxide mixtures of three systems: a. Cu(II), Bi(III), Sn(II); b. Cu(II), Bi(III), Sb(III); and c. Cu(II), Bi(III), Zn(II) were prepared, firstly, by single-element precipitation and, secondly, by co-precipitation. Thereafter, all mixtures were reduced by using hydrogen gas. Both, the initial mixtures and the reduced samples were studied by X-ray diffraction, optical and scanning electron microscopes. The chemical compositions of the precipitates were determined experimentally and their dependence on the pH was verified. It was found that alloying occurred during the reduction procedure, but in some cases the reduction was not complete (i.e. oxide phases rest in the samples). This might be a huge obstacle to use such an approach for the preparation of lead-free solders. Moreover, the materials obtained after reductions apparently are bulk alloys, thus, the preparation of small-sized metal particles would be a challenge. Another key feature to be addressed in future studies is the correlation between the chemical compositions of the parent solution and these of the corresponding precipitates.

Keywords: Cu–Bi–Zn; Cu–Bi–Sn; Cu–Bi–Sb; Ternary systems; Lead-free solders precursors; Hydroxide mixtures; Precipitation; Co-precipitation; Reduction.

[#] Corresponding author: gpvassilev@excite.com

1. Introduction

It is well known already that the high toxicity of lead is the reason to stop the use of lead-bearing solders. Nevertheless, the demand of electronics, automotive and other industries for lead-free solders can still not be fully satisfied. Thus, studies on new lead-free solders and corresponding production techniques are under way [1]. In this connection, various methods have been reported in the literature [2–6] which aim at producing particles of either pure metals or of metal-containing compounds (e.g. oxides, chalcogenides etc.) in solution. Certainly, a full review of these reports is out of the scope of this work.

Copper substrates are regularly used in microelectronic packaging, but copper is also frequently used as a constituent of multi-component lead-free solders. Nearly all of the modern solder materials are currently based on tin and this is expected to remain so for the foreseeable future. On the other hand, the use of bismuth in microelectronic solders is also prospective, and this is especially valid for a series of lead-free high-temperature solders that are now under development.

Taking into account these considerations, Bi–Cu–X (X=Sn, Sb and Zn) lead-free high-temperature solders were synthesized recently by Takaku et al. [7] using a gas-atomization method. Nevertheless, this method requires complicated technology, and therefore it would be important to continue seeking alternative ways to synthesize nano- or micro-sized solders by methods which might be easier to employ. In the past we have acquired some experience

in this field, as recently one of the authors studied the possibilities to synthesize nano- and micro-particles in the binary systems Co–Bi and Ni–Bi [8,9]. The purpose of the present studies was to acquire preliminary knowledge of a wet-chemical technique for an inorganic synthesis of lead-free solder precursors.

2. Experimental

The synthesis started initially with the precipitation of single-element hydroxides (i.e. the hydroxides of Cu(II), Bi(III), Sn(II), Sb(III), and Zn(II); see Section 2.1) to prepare ternary mixtures. In the second stage (Section 2.2), a co-precipitation of the hydroxides of three elements (i.e. the hydroxides of Bi(III) + Cu(II) + Sn(II), Bi(III) + Cu(II) + Sb(III), and Bi(III) + Cu(II) + Zn(II)) was done. Both experimental approaches were similar, but for the sake of simplicity, the two cases will be discussed consecutively. In both cases, the precipitates were reduced with pure hydrogen gas (Section 2.3).

2.1. Preparation of ternary mixtures using single-element Cu(II), Bi(III), Sn(II), Sb(III) and Zn(II) hydroxides

Pure substances (p.a.) $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, SbCl_3 , and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used to prepare 1 M solutions. Thereafter, 20 cm³ of each solution were mixed with 10 cm³ of a 3 M aqueous NaOH solution to achieve precipitation of the pertinent single-element hydroxide. The precipitates were collected in a Büchner funnel and desiccated at a

temperature of 105°C for 24 h. Ternary specimens with pre-determined metal ion contents were obtained by mixing corresponding amounts of the dry hydroxides and their compositions are listed in Table 1. The chemical compositions of the samples (concerning the metallic elements only) are plotted in Fig. 1A–C, where isothermal sections of the ternary Bi–Cu–Sn, Bi–Cu–Sb and Bi–Cu–Zn are represented. These samples were then subjected to the chemical reduction procedure by hydrogen gas as described in Section 2.3 and the products were investigated by powder X-ray diffraction (XRD), optical microscopy (OM), and scanning electron microscopy (SEM).

Table 1. Compositions of samples prepared from mechanical mixtures of single-element hydroxides (referred to the metallic elements content).

Sample No.	System	Bi at.%	Cu at.%	Sn at.%
1	Bi–Cu–Sn	18.9	66.1	15
2		12.7	76.2	11.1
3		30.9	57.9	11.2
4		25.4	63.7	10.9
5		45.2	46.8	8.0
		Bi at.%	Cu at.%	Sb at.%
6	Bi–Cu–Sb	23.6	48.1	28.3
7		23.4	51.4	25.2
8		33.4	42	24.6
9		25.7	64.8	9.5
10		41.6	10.9	47.5
		Bi at.%	Cu at.%	Zn at.%
	Bi–Cu–Zn			
11		27	37.4	35.6
12		51.2	25	23.8

2.2. Preparation of ternary mixtures by co-precipitation of {Cu(II)+ Bi(III)+X} hydroxides {X= Sn(II), Sb(III) or Zn(II)}

Ternary aqueous solutions with predetermined metal contents were prepared first. For this purpose, weighed amounts of the pure salts were dissolved in 20 cm³ water together. The chemical compositions of the ternary solutions (referred to the metal content) are shown in Table 2 (see Fig. 1A–C as well).

Co-precipitation was done by adding 10 cm³ of a 3M NaOH solution to 20 cm³ of each ternary solution. The pH value of the solution was measured after the precipitation by means of a pH-meter (HANNA). It is well known that the hydroxides Cu(OH)₂, Bi(OH)₃, Zn(OH)₂, Sb(OH)₃, and Sn(OH)₂ precipitate in different pH intervals [10], i.e. 5.5–10.0; 2.0–7.0; 7.0–8.8; 0.0–6.0 and 2.0–3.4, in the same order. As a consequence, the chemical compositions of the precipitated hydroxide mixtures might not correspond exactly to the chemical compositions of the pertinent three-element aqueous solutions.

In order to test quantitatively for possible differences, three solutions (Table 2, Nos. 18, 22, 24, i.e. one of each system) were chosen for a more detailed investigation. Thus, both the precipitated hydroxides as well as the remaining aqueous solutions were subjected to quantitative chemical analyses. These particular compositions (e.g. Nos. 18, 22, 24) were chosen in agreement with the ternary phase diagrams of the respective systems (Bi–Cu–Sn, Bi–Cu–Sb or Bi–Cu–Zn) assessed by Takaku et al. [7] so that the alloys, obtained after reduction, would lie in

Table 2. Chemical compositions (referred to the metal content) of the ternary solutions used for co-precipitation; samples used for subsequent reduction are marked.

Sample No	System	Bi at. %	Cu at.%	Sn at.%	Reduction temperature °C	Remarks
14 ^a	Bi–Cu–Sn	35.9	47.3	16.8	430	no sticking observed
15		26.5	60.1	13.4		
16		52.3	36.7	11		
17		45.6	42.9	11.5		
18 ^a		67	26	7	430	sticking observed
		Bi at. %	Cu at.%	Sb at.%		
19 ^a	Bi–Cu–Sb	35.3	31.7	33	430	no sticking observed
20		39.4	32.4	28.2		
21 ^a		51	24	25	430	no sticking observed
22		45.7	43	11.3		
23		53.9	5.3	40.8		
		Bi at. %	Cu at.%	Zn at.%		
24 ^a	Bi–Cu–Zn	49.3	25.7	25	350	sticking observed
25 ^a		73.4	13.5	13.1	390	sticking observed

^a samples undergone reduction

the liquid miscibility gaps appearing in the respective ternary phase diagrams (Fig. 1A–C). In such a way, a natural composite structure of the solder materials might be formed at solidification, under the condition of the existence of a (stable or metastable) miscibility gap. It should be mentioned that recently Manasijevic et al. [11] investigated the Bi–Cu–Sb phase diagram experimentally and performed a CALPHAD-type optimization. In their study, no liquid miscibility gap was discovered; however, they did not especially look for it. Therefore its existence is not ruled out entirely for the present investigation. Any further discussion on this topic would be out of the scope of this work.

The three-component co-precipitates were treated in the same way as described in Section 2.1. The dried masses were around 5g in each case. Thereafter, reduction by hydrogen gas was performed. The obtained products were again characterized by powder XRD, OM, and SEM.

2.3. Reduction

After some preliminary experiments, a standardized reduction procedure (as described in Table 3) was established. As one can see, it recommends a preliminary oxidation heating, i.e. converting the hydroxides to oxides of the corresponding elements, before the reduction step. This is

Table 3. Optimized procedure for oxidation and reduction of the specimens ^a

Step No.	Operation	Duration	Treatments and conditions
1	Weighing and charging the reactor. (The sample mass was about 20 g.)	15 min	Preparation of the apparatus. Room temperature.
2	Oxidation Heating		
	a) Preliminary	15 min	Oxygen flow of 100 cm ³ .min ⁻¹ ; increase of the temperature up to 300°C
	b) Initial	120 min	Oxygen flow of 100 cm ³ .min ⁻¹ , 300°C
	c) Transitional	10 min	Oxygen flow of 100 cm ³ .min ⁻¹ , increase of the temperature from 300 to 400°C
	d) Main	120 min	Oxygen flow of 100 cm ³ .min ⁻¹ , 400°C
3	Reduction Heating		
	a) Preliminary	15 min	Inert gas flow of 100 cm ³ .min ⁻¹ , 430°C
	b) Main	240 min	Hydrogen flow of 100 cm ³ .min ⁻¹ , 430°C
4	Passivation		
	a) Preliminary	20 min	Hydrogen flux of 100 cm ³ .min ⁻¹ , cooling from 430°C to room temperature
	b) Main	10 min	Mixed flux (10% oxygen in inert gas) of 100 cm ³ .min ⁻¹ , room temperature
5	Retrieving of the specimen and weighing	10 min	Dismounting of the reactor, conservation of the specimen.

^a These experiments were performed (under hire) in the Institute of Kinetics and Catalysis, Bulgarian Academy of Sciences.

necessary in order to remove the hydrogen contained in the hydroxides so that no water vapors are formed during the reduction.

2.4. Chemical analyses

The chemical compositions of the precipitated three-element hydroxides had to be determined experimentally since the solubility product (i.e., the solubility) of every hydroxide depends on the pH value in a different way. Quantitative analyses of the Bi and Cu content in the precipitates were done by volumetric and gravimetric

methods, respectively. For the determination of Bi, around 0.03 g of the dry precipitate mixture were dissolved in concentrated nitric acid (0.7 cm³). Water was added to adjust the volume to 10 cm³. The solution was titrated by EDTA (complexon III) using xylenol orange as indicator. Five parallel analyses were performed each time in order to obtain a statistically reliable mean value. For the determination of copper, samples of around 0.58 g of the hydroxide mixture were weighed, dissolved in nitric acid (2:1) and subjected to a standard electrochemical deposition procedure. The each content of

the corresponding third element (Zn, Sb, or Sn) was obtained from the corresponding difference in mass.

2.5. Samples characterization

The samples were characterized by powder X-ray diffraction (XRD) on a Bruker D8 powder diffractometer equipped with a high speed LynxEye one dimensional silicon strip detector and a Cu X-ray tube. The patterns were analyzed using the 'Topas 3' software (Bruker AXS, Karlsruhe, Germany). Crystal structure data for phase identification were taken from Pearson's Handbook of Intermetallic Phases [12].

A representative number of samples were also investigated by scanning electron microscopy using a JEOL JSM-6460 apparatus with EDAX analyzer.

3. Experimental results and discussion

White (for Sn(II), Sb(III), Zn(II)) or blue (for Cu(II)) colored precipitates were obtained after adding the alkaline solution. In the case of bismuth, a light-yellow precipitate was obtained, probably due to the spontaneous dehydration of $\text{Bi}(\text{OH})_3$ to $\text{BiO}(\text{OH})$. In addition, it was also observed that $\text{Sn}(\text{OH})_2$ changed color from white to grey during filtration and even to dark-grey after heating at 105°C . A similar phenomenon was also observed during desiccation heating of $\text{Cu}(\text{OH})_2$. This could be explained by a gradual dehydration of the corresponding hydroxides and the formation of SnO or CuO [13], respectively. Nevertheless, these processes do not influence the ratio of the metallic elements

that was determined experimentally.

Concerning the experiments described in Section 2.2, white precipitates were observed during the dissolution of the Bi(III)-, Sn(II)- and Sb(III) salts. This phenomenon is easily understood, taking into account the above mentioned pH intervals of precipitation. It could be avoided for Sn(II)- and Sb(III)-containing samples by using concentrated hydrochloric acid due to formation of soluble chloride complexes, ($[\text{SnCl}_4]^{2-}$ and $[\text{SbCl}_4]^-$, respectively).

The following observations concern some effects due to the sequence of mixing. They were observed when co-precipitations were done. Firstly, when Sn(II) solution was added to the Bi(III) containing beaker, then the color of the common precipitate became yellow (possibly due to the formation of $\text{BiO}(\text{OH})$). Another explanation might be that Sn(II) acts as reducing agent to Bi(III), reducing it to Bi(0). Indeed, the standard potentials of the redox couples Sn(II)/Sn(IV) and Bi(0)/Bi(III) have values of +0.151 V and +0.308 V, respectively [13], and the overall redox potential of the reaction $3\text{Sn}(\text{II})+2\text{Bi}(\text{III})=3\text{Sn}(\text{IV})+2\text{Bi}(\text{0})$ is actually positive. Anyhow, the experiments have shown that the sequence of adding the components had to be changed to bismuth-copper-tin (solutions). Finally, the measured quantities of aqueous NaOH solutions were added in portions until the pH value became about 8 to 9. Such a pH is needed to assure the precipitation of $\text{Cu}(\text{OH})_2$.

When co-precipitating Bi(III)-, Cu(II)-, Sb(III) hydroxides, it was found that one should mix Bi- and Cu-solutions first in order to achieve proper results. The reason is

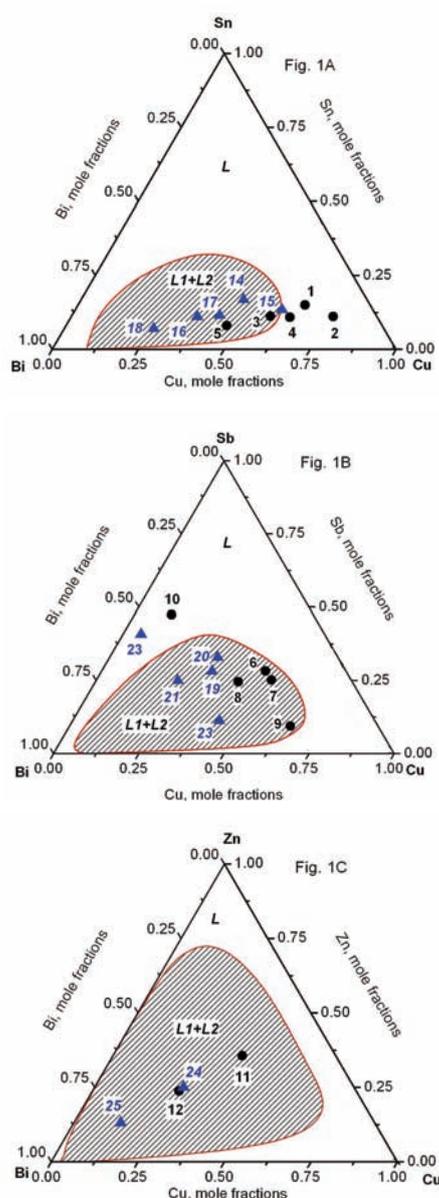


Fig. 1A–C. Tentative isothermal sections of the ternary phase diagrams Bi-Cu-Sn (Fig. 1A), Bi-Cu-Sb (Fig. 1B) and Bi-Cu-Zn (Fig. 1C) at 650 °C. L – Liquid phase. The miscibility gap probably metastable areas (L1+L2) are suggested by Takaku et al. [7]. The circles (●) represent the samples composition (up to Table 1), the triangles (▲) – chemical compositions of the ternary solutions (referred to the metal content) as shown in Table 2. Solidus and liquidus lines are not represented in Figs 1 A-C.

that if $\text{Sb}(\text{OH})_3$ precipitates first (this occurs at $\text{pH}=0$), it sticks to the glass wall, and large weight losses could occur.

Six of the co-precipitated three-element samples (i.e. two of each system studied) were subjected to the reduction process (Nos. 14, 18, 19, 21, 24, 25, Table 2), applying the procedure described in Table 3. Some challenges concerning the reduction were encountered. Namely, the reaction under hydrogen flow had to be performed at relatively high temperature (i.e. 430°C, see Table 3) in order to obtain effective reduction. Higher temperatures were not available due to limitations by the reactor's materials. Moreover, it is known that some of the elements exhibit lower melting points (e.g. Zn at 419.6°C, Bi at 271.3°C, Sn at 232.0°C [14]). This seemed to pose no problems except for zinc-containing specimens where overheating used to occur in the reactor, made of thermal glass. In such a case, the sample became partially liquid, sticking firmly to the reactor wall and breaking it on cooling. That is why the reduction of such risky samples was performed at 390°C. Even then, the appearance of a liquid phase sticking to the reactor walls was frequently observed. This was obviously caused by additional heating by the heat deliberated in the alloying reactions between liquid Zn and solid Cu (Cu–Zn intermetallic phases exhibit large negative enthalpies of formation [15]).

A short literature review of the Sn, Bi, Zn, Sb, and Cu oxides and hydroxides thermal stabilities is given in Table 4. It is evident that the chosen desiccation temperature of 105°C is low enough in order not to activate decomposition of the pertinent hydroxides.

After reduction various samples were investigated by SEM. It was found that the particles, consisting initially of single elements, had obviously reacted with each other forming microcrystals of the corresponding alloys. As an example, a SEM micrograph of sample No. 6 (Bi–Cu–Sb) is represented in Fig. 2. Three points of the sample were analyzed in order to obtain the local chemical compositions, and the results are listed in Table 5. One ought to be aware that the Bi–Sb alloys exhibit complete

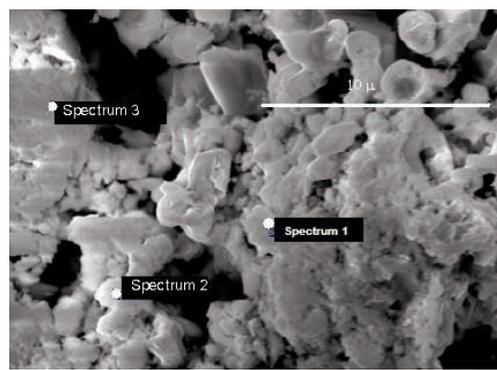


Fig.2. Micrograph of sample No.6 (belonging to the Bi-Cu-Sb system). The points where SEM analyses were done are indicated.

Table 4. Review of some physico-chemical properties of Sn, Bi, Zn, Sb, and Cu oxides and hydroxides, Ref. – literature source, K_S – solubility product, S – solubility

Oxides and hydroxides formulae	Notes	Ref.
Bi_2O_3	Yellow	[16]
Bi_2O_5	Red–brown	[16]
$\text{Bi}(\text{OH})_3$	White. Decomposes at about 100°C to $\text{BiO}(\text{OH})$ and at higher temperature to Bi_2O_3 . $K_S = 3.2 \times 10^{-32}$; $S = 3 \times 10^{-9} \text{ mol.l}^{-1}$	[16]
Cu_2O	Yellow or red, depending on the precipitation technique	[18]
CuO	Black. Decomposition at 1100°C	[18]
$\text{Cu}(\text{OH})_2$	White–blue. Decomposes at 185°C . $K_S = 2.2 \times 10^{-2}$; $S = 1.48 \times 10^{-3} \text{ mol.l}^{-1}$	[18]
ZnO	White	[17]
$\text{Zn}(\text{OH})_2$	White. Decomposition at 125°C . Existing in various modifications. $K_S = 7.1 \times 10^{-18}$. $S = 2.6 \times 10^{-6} \text{ mol.l}^{-1}$	[17]
Sb_2O_3	White at room temperature, yellow – on heating	[16]
Sb_2O_5	White–yellow. Decomposition at temperatures above 350°C	[16]
$\text{Sb}(\text{OH})_3$	White. No literature data about the decomposition temperature. K_S – no data.	[16]
SnO	Black. Decomposition at temperatures above 550°C	[16]
SnO_2	White. No literature data about decomposition temperature	[16]
$\text{Sn}(\text{OH})_2$	White. No literature data about the decomposition temperature. $K_S = 6.3 \times 10^{-27}$; $S = 7.9 \times 10^{-11} \text{ mol.l}^{-1}$	[16]

solubility both in liquid and in solid state while in the Cu–Sn system a number of intermediate phases are formed [14]. The results indicate that metastable alloys (supersaturated in copper) might have formed during the reduction process.

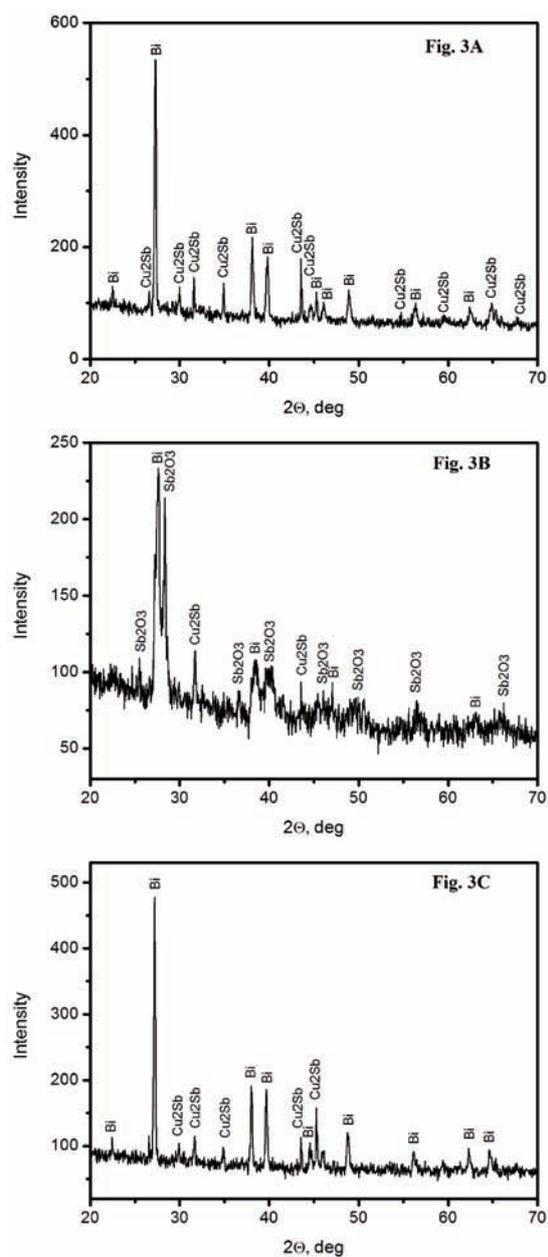
Most of the reduced samples were checked for their phase composition by powder XRD. Figs. 3A–C show powder patterns of three reduced Bi–Cu–Sb samples as examples (No. 8, 10, and 21, respectively). It can be seen that two of them (Fig. 3A and 3C) were obviously metallic with two separate phases present, i.e. (Bi, Sb) solid solution plus Cu_2Sb (in basic agreement with the phase diagram by Manasijevic et al [10]), whereas sample 10 (with the highest Sb content) showed also a high content of Sb_2O_3 (Fig. 3C) which had obviously developed in the process of preparation, possibly due to an insufficient reduction step.

Table 5. Results of SEM analyses with the reduced sample No. 6

Spectrum	Bi at. %	Cu at. %	Sb at. %
Spectrum 1	2.5	17.5	80
Spectrum 2	1	28.6	70.4
Spectrum 3	17.5	24.7	57.8

All XRD results are collected in Tables 6 A–C where the compositions are estimated from the calculated diffraction line intensities. It is obvious that in the first series of samples in the systems Bi–Cu–Sn and Bi–Cu–Sb (Nos. 1–10) which had been prepared by a reduction of a mixture of the individual oxides the pure elements were still present, and only part had reacted to form intermetallic compounds. Sometimes, there

are also rather high oxide contents in the samples probably due to insufficient reduction, with the highest oxide contents in sample 5 with 64.3 % Bi_2O_3 (this sample was also richest in Bi) and sample 10 with 50.9 % Sb_2O_3 (again this sample was richest



Figs. 3A–C. Diffractograms of the reduced samples 8, 10 and 21, respectively.

Table 6 A. Composition of the reduced Bi–Cu–Sn samples assessed by powder XRD. The numbers given in the Table are percentages of the calculated powder pattern intensity

Sample No.	Bi %	Cu %	Sn %	Cu ₃ Sn %	Cu ₁₀ Sn ₃ %	Bi ₂ O ₃ %	SnO ₂ %
1	25.2	28.3	5.5	24	–	–	17
2	20.4	46.8	2.7	27.4	–	–	2.7
3	32.9	28.9	5.5	14.8	7.6	10.3	–
4	26	39.3	3.7	13.2	10.1	7.7	–
5	14.7	–	2.3	8.6	10.1	64.3	–
14	61.9	–	–	17.9	–	–	20.2
18	26.1	–	–	12.3	–	61.6	–

Table 6B. Composition of the reduced Bi–Cu–Sb samples assessed by powder XRD. The numbers given in the Table are percentages of the calculated powder pattern intensity

Sample No.	Bi ^a %	Sb %	Cu ₂ Sb %	Cu ₁₁ Sb ₃ %	Sb ₂ O ₃ %
6	24.1	–	50.5	–	25.4
7	29.8	11.1	54	–	5.1
8	73.5	–	26.5	–	–
9	47	–	–	53	–
10	42.7	–	6.41	–	50.9
19	55.7	–	44.28	–	–
21	57.8	–	42.18	–	–

^a (Bi,Sb) solid solution

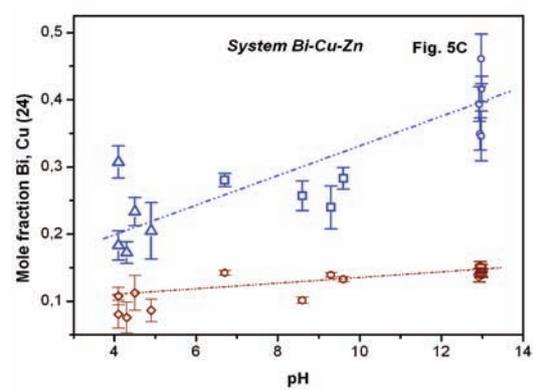
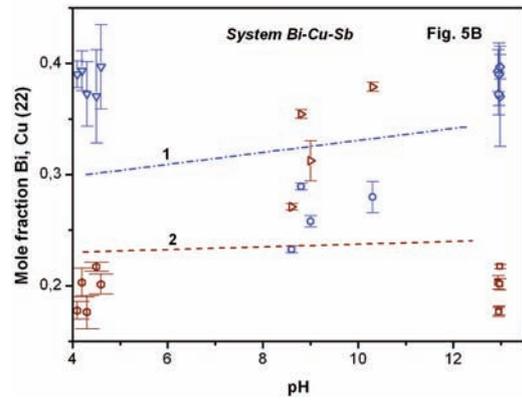
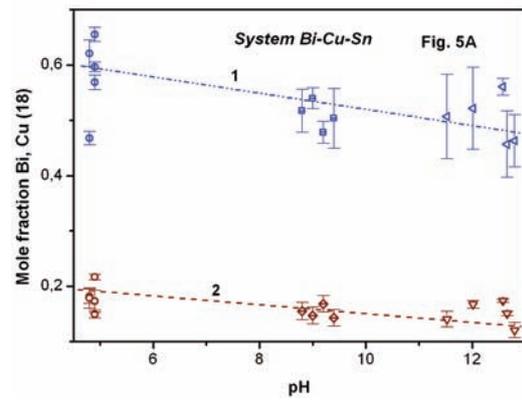
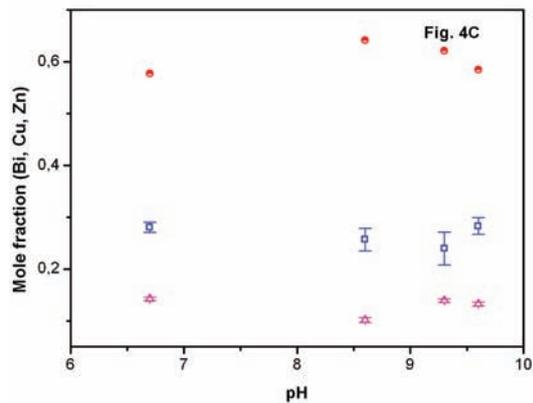
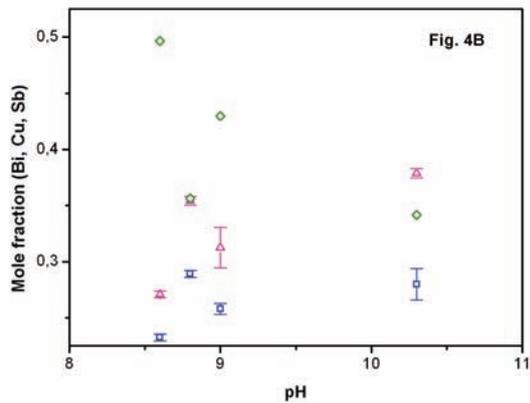
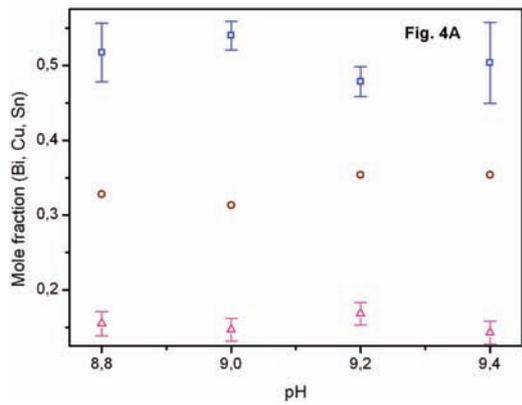
in Sb). In the Bi–Cu–Sn samples that had been obtained by co-precipitation and reduction were still observed considerable contents of oxides, with the highest content of Bi₂O₃ in sample 18 (61.6 %) which was also the Bi-richest of all. It is interesting to note that the two Bi–Cu–Sb samples, obtained by co-precipitation and reduction, consisted apparently only of (Bi, Sb) and Cu₂Sb as was to be expected from the phase diagram [10]. It is of worth noting that the latter two ternary systems are subject of further studies [19, 20] thus confirming the actuality of the present work.

Table 6C. Composition of the reduced Bi–Cu–Zn samples assessed by powder XRD. The numbers given in the Table are percentages of the calculated powder pattern intensity

Sample No.	Bi %	Cu %	Bi ₂ O ₃ %	ZnO %
11	17.9	22.7	16	43.4
12	11.5	12.8	18.2	57.5
24	58.1	25.4	–	16.5
25	14.5	4.9	65	6.6

All samples containing Zn (Nos. 11, 12, 24, and 25) contained also very high amounts of oxides (Bi₂O₃ and ZnO), practically independent of their method of preparation.

The chemical compositions of the solid samples (hydroxides) were determined by chemical analyses (see Paragraph 2.4). Experimental data of the pH values of the residual solutions (i.e. after precipitation) of samples 18, 22 and 24, respectively, with stoichiometric quantities of NaOH are shown in Figs. 4 A–C, combined with results of the samples chemical compositions. The contents of the corresponding third element (Zn, Sn or Sb) are assessed from the mass difference. As one can see, the Bi and Cu contents of the precipitates do not vary significantly with pH for the systems



Figs. 4A–C. Experimental pH of the parental solutions (after precipitation with stoichiometric quantity of NaOH) versus chemical compositions of samples 18 (Bi-Cu-Sn system), 22 (Bi-Cu-Sb system) and 24 (Bi-Cu-Zn system), respectively. The symbols (\square) and (\triangle) show the mol fractions (in the precipitate) of Bi and Cu, in the same order. The contents (o) of the third element (i.e. Sn, Sb or Zn, respectively) are assessed.

Figs. 5A–C. Experimental pH of the parental solutions versus chemical compositions of samples 18, 22 and 24, respectively. On the left side are exhibited cases precipitated with a deficit of 20 % NaOH, and on the right side – with an excess of 20 % NaOH. In the middle are represented results of the samples precipitated with stoichiometric quantity of NaOH. Line 1 and line 2 correspond to the overall bismuth and copper content, respectively, obtained in all samples.

Bi–Cu–Sn (Fig. 4A) and Bi–Cu–Zn (Fig. 4C). For the system Bi–Cu–Sb a noticeable increase of the Sb content can be observed with decreasing pH values (Fig. 4B). However, a correlation with the pH intervals of precipitation of the respective hydroxides could not be established.

Precipitations with excess (20 %) and substoichiometric (20 %) quantities of NaOH were performed for samples 18, 22 and 24 as well (Fig. 5A–C). As one can see, the compositions of the (solid) samples change smoothly with pH (corresponding the added quantity of NaOH) in the case of the Bi–Cu–Sn and Bi–Cu–Zn, while, again, an “irregular” behavior is observed for the system Bi–Cu–Sb (see Fig. 5B). Lines 1 and 2 correspond to the average bismuth and copper content, respectively, obtained in these samples.

4. Conclusions

For the sake of the preliminary studies on the design of lead-free solders attempts of ternary hydroxide mixtures preparations and their reduction were done. The following systems are concerned: a. Cu(II), Bi(III), Sn(II); b. Cu(II), Bi(III), Sb(III); and c. Cu(II), Bi(III), Zn(II). The precipitates were reduced by using hydrogen gas but some challenges appeared (e.g. the reduction is not always complete and the particles size could not be controlled). X-ray diffraction, optical and scanning electron microscopes studies have shown the predominant metallic character of the reduced materials. However, the frequently incomplete reduction might be a huge obstacle to use such an approach for the preparation of lead-free solders.

The chemical compositions of the precipitates were sensitive to the pH value of the solutions. Bi and Cu contents of the precipitates do not vary significantly with pH for the systems Bi–Cu–Sn and Bi–Cu–Zn while for system Bi–Cu–Sb a noticeable increase of the Sb content can be observed with decreasing pH values.

When excess and sub-stoichiometric quantities of NaOH were applied for the precipitation, the compositions of the (solid) samples change smoothly with pH (i.e. proportionally to the added NaOH) in the case of the Bi–Cu–Sn and Bi–Cu–Zn, while, again, an “irregular” behavior is observed for the system Bi–Cu–Sb (hydroxides). Nevertheless, the correlation between the chemical compositions of the parent solution and of the corresponding precipitates is a topic that needs further studies as well.

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