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Formation of particles of bismuth-based binary alloys and intermetallic compounds by ultrasonic cavitation

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Abstract

This work describes the interactions of molten bismuth with other low-melting point metals (Sn, In, Ga and Zn) under sonication. Binary combinations of bismuth and one of these metals were melted together in hot silicone oil and irradiated with ultrasonic energy to form micro/nano alloy particles. The morphology, composition and crystal structure of these particles were analyzed. It was found that bismuth forms metal matrix composite with tin and zinc, intermetallic compounds with indium and an alloy with gallium. We also followed the structural changes in the system by X-ray diffraction (XRD), Differential scanning calorimetry (DSC), and electron microscopy.

Keywords: ultrasonic, microspheres, alloy, Bi-In, Bi-Ga, Bi-Sn, Bi-Zn, intermetallic, metal matric composites.

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Introduction

The fabrication and study of nanoparticles of metal-based alloys is an active area of nanotechnology research. The large variety of alloy nanoparticle compositions results in a rich spectrum of structures, morphologies, properties and potential uses [1, 2]. In general, alloys are mixtures or metallic solid solutions containing two or more elements. They are composed of one or more of the three kinds of structures: a solid solution of the elements (a single phase), a mixture of metallic phases (two or more solutions) and an intermetallic compound with no distinct boundary between the phases. Alloys in the form of micro-/nano-particle may exhibit superior properties over bulk alloys while changes in their compositions may fine-tune their attributes [3]. Binary and ternary alloy nanoparticles were investigated for basic research, such as studying the size effect on the stability and reactivity of nanoparticles [4-6], as-well-as for possible applications. Binary alloy nanoparticles are used for the formation of semiconductor nanowires, and their properties are intensely investigated as they provide the basis for tailoring vapor-liquid-solid growth to achieve complex one-dimensional materials geometries [7]. Nanoparticles of alloys can have different phase behavior, such as solubility of one of the components, melting and crystallization, very different from the corresponding bulk alloys [8]. Ternary alloy nanoparticles are of interest as they might, for instance, provide a facile pathway for incorporation of dopants in nanoscale structures such as nanowires and controlled modification of the surface of the nanowire by an ordered carbon shell leads to drastic changes in the solubility [9].

Micro- and nano particles of alloys were prepared by various methods (like as laser ablation, ultrasonic, sol-gel, hydrothermal, etc.). Formation by laser ablation of bulk alloys was reported by few research groups [10, 11]. Ultrasonic energy was also utilized for the preparation of nanoalloys. Chen et al.[12] irradiated a solid granule of solid Sn-Bi alloy, immersed in paraffin

oil at room temperature, using a high intensity ultrasonic probe. Melting of the solid alloy eventually occurred when the oil was heated due to the sonication. The resulting particles were analyzed by X-ray diffraction (XRD) and exhibited phases corresponding to Sn and Bi. The size distribution of the particles was found to decrease as the ultrasonic power was raised, within the range of 10-80 nm. Formation of alloy nanoparticles by ultrasonic energy was reported also by Han et al. [13]. They have irradiated molten Field's metal (Bi-In-Sn alloy) in silicone oil containing a surfactant, and obtained stable nanoparticles of this alloy in the size range of 15 nm. The same was done with pristine indium metal. We have used ultrasonic energy to form micro-and nanoparticles of some low melting-points metals as-well-as of two eutectic alloys (Au-Ge, Au-Si), after melting them in silicone oil [14].

Recently we reported on the formation of gallium microspheres by ultrasonic irradiation of molten gallium in either water or in silicone oil [15-17]. Performing this process in aqueous solutions of metallic ions (Ag, Cu, Au) that have more positive reduction potentials than gallium resulted in instantaneous reduction of these ions by Ga and formation of intermetallic compounds (Ag₂Ga, CuGa₂ and AuGa₂) in the form of particles [18]. In the present work we describe the formation of particles of binary alloys composed of bismuth and other low m_p metals (Sn, In, Ga, Zn).

Experimental

Chemicals: Silicone oil (polyphenyl methysiloxane) AP 100 (Fluka), [1.062 g/mL (20 °C), 100 mPa (neat, 25 °C)] was used as received. Bismuth (99.99%), indium (99.9%), tin (99.98%) gallium (99.99%) and zinc (99.998) metals were purchased from Sigma-Aldrich and used as received. **Experimental procedure:** In a typical experiment, granules of the two metals (0.1-0.5 g each) were placed in a quartz test tube (6 cm long, 13 mm in diameter) with a conical bottom. 3 mL of silicone oil were added, and the test tube was gently heated using a small portable gas burner.

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Substantial decomposition of the oil was observed above 410 °C. When the two metals were molten ultrasonic radiation was applied at 20 kHz for 2 minutes using an ultrasonic transducer of 100 W, while still being heated. Dispersion of the molten metals particles in the oil occurred as soon as the acoustic field was applied. The test tube was heated for another 2 minutes and then was let to cool to room temperature. The sample was transferred into a centrifuge test tube containing n-hexane, a good solvent for the oil, and spun down at 8000 rpm for 10 min. After decantation of most of the liquid, another portion of n-hexane was added, followed by washing and centrifugation. This procedure was repeated twice to replace all the Si-oil by n-hexane, in which the metal particles were kept to prevent oxidation.

Equipment: The Ultrasonic transducer was produced by ultrasonic transducer (model VCX 750, frequency 20 kHz, volt 230V AC) was obtained from Sonics and Materials Inc., USA. SEM Images were recorded using a Gatan US1000 CCD camera. SEM images were obtained with FEI Inspect microscope model S, operated at 30kV. A small droplet sample was applied on a SEM sample holder, coated with a carbon tape, and the water was evaporated at ambient atmosphere. No gold coating of the sample was needed due to the good conductivity of the metallic particles. DSC measurements were performed with a NETZSCH leading thermal analysis, DSC 200 F3 Maia using the liquid nitrogen operating at -100 °C to 500 °C. The N₂ purging flow was 40ml/min and the heating rate was 5K/min. X-ray diffraction (XRD) measurements were performed with a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation operating at 40 kV/30 mA with a 0.02 step size and a 1 s step. Elemental analysis was performed using the SEM energy dispersive X-ray spectroscopy (EDS). Raman spectra of Bi-In were recorded on Renishaw inVia Raman microscope equipped with RL785 and RL830 Class 3B wavelengthstabilized diode lasers and Leica DM2500 M (Leica Microsystems) materials analysis microscope. A sample was prepared by applying a small sample of the powder of Bi-In

nanoparticles on a glass slide. A spectrum could be obtained by focusing the instrument lens on the sample and irradiating it with 514 nm laser.

Results

Bismuth-Tin particles

A mixture of 0.530 g bismuth (2.54 mmol) and 0.462 g tin (3.89 mmol) was melted in silicone oil in a quartz test tube. This composition (39.5 at% Bi, 60.5 at% Sn) is close to that of the eutectic alloy Bi-Sn (43 at% Bi, 57 at% Sn). The molten mixture was irradiated with ultrasonic energy, as described in the experimental section, forming a grey suspension of particles in the oil. After precipitation, the particles were separated, washed several times with n-hexane and dried. SEM images of the particles show spheres of sub-micron to several microns in diameter. Each of the spheres exhibits segregation of the two metals, which appears as bright features on the dark spheres (Fig. 1A). Careful examination of the images reveals two patterns of segregation: on the surface of the large sphere in Fig. 1B, a lamellar pattern is observed, which is characteristic of a well phase-separated solid eutectic.



Fig. 1: SEM images of Bi-Sn particles formed by ultrasonic cavitation of a mixture of molten bismuth and tin in Si- oil. Inset: EDS spectrum of the area shown in Fig. 1B.

The bright lamellae correspond to the heavier element, Bi in this case. EDS analysis of the particles (Fig. 1A inset) indicates the existence of these two elements only: a single peak for Bi and two peaks for Sn. Elemental mapping of the area shown in Fig. 1A provides the distribution of Bi (Fig. S1A, see the supporting information) and of Sn (Fig. S1B, see the supporting information). Matching these images with Fig. 1B reveals almost even distribution of the elements, whereas the bright features on the surface are consisted of Bi. Since the initial atomic composition of the sample contained ca. 20% more Sn, and since the Bi mostly appears as separate features on the surface, this kind of heterogeneous alloy can be considered as a metal matrix composite (MMC) where the tin is the matrix and the bismuth is the reinforcement.

X-ray analysis of these particles (Fig. 2) shows multiple peaks, all matching with the database for either elemental Sn or Bi. No other peaks that correspond to any compound consisted of these elements are observed. The existence of each metal in its typical crystalline form supports the suggested type of heterogeneous alloy, where on the microscopic level each metal retains its identity but as a bulk the macroscopic properties, such as the melting point, are different than those of the individual metals (vide infra).



Fig. 2: X-ray diffractogram of the Bi-Sn particles, showing the matching of the peaks with the database of pure Bi (red) and Sn (blue).

DSC analysis of the Bi-Sn particles in the temperature range of 0-500 °C (Fig. 3) shows a single sharp endothermic peak with an onset temperature of 136 °C and a single exothermic signal on the cooling scan. This melting temperature is slightly lower than the eutectic point (figure S2, see the supporting information) of the Bi-Sn alloy (139 °C). This proximity indicates that the bulk of the particles are of eutectic composition. The small deviation is due to the slight melting-temperature depression that occurs with such particles in the micrometric to sub-micrometric dimensions [19]. This effect becomes more dramatic as the particles' sizes approach the nanometric scale [20]. No melting signal were observed for either of the composing metals separately, although they were found to retain their individual crystalline structure and although their melting temperatures (Bi: 271.3 °C, Sn: 231.9 °C) are within the range of this measurement (figures S3 and S4, see the supporting information). Altogether the results exhibit the dual nature of the metal matrix composite: On one hand, upon heating and cooling it behaves as an alloy. On the other hand, the SEM images and the X-ray pattern indicate segregation of the two components. It can be concluded that the Bi-Sn particles are a two-phase heterogeneous alloy.



Fig. 3: DSC analysis of the Bi-Sn particles, showing a single melting signal. Starting temperature: 0° C. The onset temperatures of the signals are marked.

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Bismuth-indium particles

Sonication of a molten mixture (50:50 wt%) of Bi-In in hot silicone oil also produced spheres in the size-range of sub-micron to a few microns in diameter. However, unlike the Bi-Sn particles, here the SEM images (Fig. 4) showed no elemental segregation or separate features on the surface of the particles. Examination of the SEM images reveals also some crater-shaped deformations and fusion of some particles, which were caused by local high temperatures that develop as a result of the energetic collisions of the solidifying particles under the microjets, created after the collapse of the cavitation bubble.



Fig. 4: SEM image of Bi-In spheres formed by ultrasonic irradiation of a molten mixture of the two metals (1:1 wt. ratio). The crater-shaped deformations and the fused spheres are marked. Inset: EDS spectrum obtained from this section of the sample.

Qualitative and quantitative X-ray diffraction analysis results are summarized in Table 1. In addition to Bi and solid solution of In with 5 % Bi, the major intermetallic compounds were BiIn and BiIn₂. The main crystallographic data of all the identified phases are given in Table 2. The qualitative (identification) and qualitative (Rietveld refinement) analyses are demonstrated in Figs 5, 6 and S5.

<u>Table 1</u> : The molar ratios of the various products obtained by ultrasonic irradiation of molten
mixtures of Bi and In of different compositions. These values were calculated from the Reitveld
refinement using two different programs (PCW and FP).

	Initial metals ratio				Reitveld	% molar of the products								
Sample	Sample weight at		ator	mic	refinement									
	Bi	In	Bi	In	remement	Bi – hR	Bi-m-12	BiIn	Bi ₃ In ₅	BiIn ₂	In (SS)			
2	3	1	0.62	0.38	PCW	67.3	0.0	11.4	0.0	4.7	16.6			
3					FP	67.3	0.0	11.7	0.0	6.1	14.9			
4	4 2	1 0.	0.52	0.48	PCW	38.4	0.0	59.7	0.0	1.9	0.0			
4			0.32		FP	39.5	0.0	58.2	0.0	2.2	0.0			
6	6 1 1 0.30	1	0.26	0.64	PCW	19.3	0.0	40.8	3.5	36.4	0.0			
0		0.50	0 0.04	FP	18.8	0.0	41.0	3.7	36.6	0.0				
7	1 2	1	1 2	2	2	0.22	0.79	PCW	0.0	3.3	73.2	0.0	23.4	0.0
/		Z	0.22	0.70	FP	0.0	4.6	71.1	0.0	24.2	0.0			
8	1	3	0.11	0.89	PCW	0.0	0.0	0.0	0.0	41.8	58.2			
					FP	0.0	0.0	0.0	0.0	34.6	65.4			

Table 2: Bi-In system: Crystal structures of alloys and compounds appeared at Table 1

Formula	Cryst. System	space group	Pearson symbol	ICDD PDF card	
$In_{1-x}Bi_x$ solid solution *	tetragonal	I4/mmm (139)	tI2	NA	
Bi	rhombohedral	R-3m (166)	hR2	5-519	
Bi	monoclinic	C2/m (12)	mC4	65-1215	
BiIn ₂	hexagonal	P6 ₃ /mmc (194)	hP6	11-566	
BiIn	tetragonal	P4/nmm (129)	tP4	32-113	
Bi ₃ In ₅	tetragonal	I4/mcm (140)	tI32	23-850	

* (x~0.05)



Fig. 5: X-ray diffraction pattern obtained from the Bi-In particles (formed from 1:1 wt ratio) with the database matching, showing the existence of $BiIn_2$ (blue), BiIn (red) and some unreacted crystalline Bi (green). Inset: Raman spectrum obtained from this sample.



<u>Fig. 6</u>: Rietveld diagram for the sonication product of the molten mixture of Bi:In 1:2 wt. ratio. Blue signals: BiIn, red signals: $BiIn_2$.

Phase explosion occurs as a result of homogeneous nucleation in a metastable melt when vapor bubbles form in the overheated liquid, ultimately resulting in the formation of nanoscale particles from the vapor and liquid droplets present in the plume [21]. During ultrasonic irradiation there is a fast rise of the temperature and pressure (6000 K, 200 atm) in the center of the collapsing bubble, with the centrally exposed portion reaching a higher temperature than the periphery. This can cause the formation of bismuth-indium intermetallic compounds, which is evidenced also from the Raman spectrum (Fig. 6 inset) that includes four peaks. The one at 97 cm⁻¹ is attributed to phonon vibration while the peaks at 126 cm⁻¹, 227 cm⁻¹ and 311 cm⁻¹ are associated with the stretching and vibration modes of the Bi-In bonds in BiIn, Bi₃In₅, and BiIn₂, respectively. The same explanation for the formation of the intermetallic compounds can be given for the Bi-Sn system, but there no intermetallic compounds were formed. The reason is that there are no intermediate phases in the Bi-Sn system and the phase diagram (Fig. S2) is typical eutectic.

Further examination of the Bi-In interactions was done by preparing particles from various ratios of the molten mixtures of the two metals and analyzing the diffraction patterns of the products using the Rietveld refinement method. Fig. 6 presents a Rietveld diagram as an example of the Rietveld analysis for the product of the Bi-In 2:1 wt. ratio (nearly equimolar mixture), showing that in this case the two main phases are BiIn and BiIn₂. The molar percentage of the phases for each composition of the melts was calculated from the Rietveld's refinement method using two programs: Powder Cell for Windows (PCW) and FullProf (FP). The results obtained from these programs were close to each other and demonstrated the effect of the initial ratio on the product distribution (Table 1 and figures S5). At all five cases both components (Bi and In) were present in the particles For example, when Bi was in a large molar excess most of it remained unreacted with only minor amounts of BiIn and BiIn₂. However, when In was in excess only the intermetallic compounds BiIn₂ and BiIn were formed. (see Table 2).

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Elmental imaging of Bi and In in the product of the 1:1 wt. mixture (0.36 Bi : 0.64 atomic ratio) shows nearly even distribution of these elements in the particles (Fig. 7). Moreover, these images appear to be complementary to each other: some sites which are depleted with one element seem to be enriched with the other element, as marked on the images.



<u>Fig. 7</u>: Elemental mapping of Bi-In spheres formed by ultrasonic irradiation of a molten mixture of the two metals (1:1 wt.). The arrows point to regions of single particles which are Bi-enriched with respect to In.

DSC analysis of the Bi-In particles that were formed from the 1:1 wt. mixture was carried out in the temperature range of 0 - 300 °C. The thermogram, (Fig. 8) shows almost similar curves on the repeating scans, with melting and crystallization temperatures far from those of the pure metals $(In_{mp}=156.6 \ ^{\circ}C \ ^{\circ}Bi_{mp}=271.4 \ ^{\circ}C)$. The heating scans exhibit large and small endothermic signals which are partially coalesced, with onset temperature of 69 $\ ^{\circ}C$ and approximately 80 $\ ^{\circ}C$, respectively. On the cooling scans separated small and large exothermic signals are observed. While the endothermic signal at ca. 88 $\ ^{\circ}C$ can be assigned to BiIn, according to the phase diagram (figure S6), the major signal that starts at 69 $\ ^{\circ}C$ may be assigned to BiIn₂. Here, too, the melting temperatures are lower than the usual ones for these phases, due to the melting-temperature depression in small particles. Two other tiny endothermic signals can be observed with onset temperatures of ca. 50 and 107 $\ ^{\circ}C$; one of them may be attributed to the minor product large particles of BiIn which was identified by XRD while the source for the other one is not clear.



Fig. 8: DSC thermogram of the Bi-In particles that were prepared from the starting composition of 1:1 Bi – In wt ratio. Starting temperature: 0° C. The onset temperatures of the signals are marked.

Bismuth-gallium particles

A mixture of 0.342 g bismuth (1.64 mmol) and 0.310 g gallium (4.45 mmol) was melted, irradiated with ultrasonic energy and separated as described above. SEM images of the product (Fig. 9) show that the particles are in the same size-range as those of Bi-Sn and Bi-In, but are not in the shapes of perfect spheres.



Fig: 9. SEM image and EDS analysis of Bi-Ga micro-/nano-particles. Inset: EDS spectrum obtained from this section of the sample.

EDS analysis indicates the presence of both elements, and elemental imaging (Fig. 10) shows complementary presence of bismuth and gallium, evenly distributed in the scanned area. However, the XRD pattern (Fig. 11) shows signals that correspond only to the database of bismuth. Based on all these data, it can be concluded that these particles are consisted of either an interstitial alloy of crystalline Bi containing trapped Ga atoms or an alloy composed of crystalline bismuth and amorphous gallium. Interstitial alloys are formed when one kind of atoms is substantially smaller than the other. In this case, however, the atomic radius of bismuth (1.43-1.70 Å) is only somewhat larger than that of gallium (1.36-1.41 Å). A similar proportion exists in the couple Bi-Zn, where the atomic radius of Zn is 1.35 Å, but the Bi-Zn diffraction pattern showed separate signals for Bi and Zn (vide infra), as in the case of Bi-Sn. It can thus be concluded that the particles are composed of a heterogeneous alloy in which only the Bi is crystalline.



Fig. 10: Elemental mapping, performed on the environmental SEM, showing the distribution of bismuth and gallium of the area shown in Fig. 9.



Fig: 11. X-ray diffraction pattern obtained from Bi-Ga particles.

Bismuth-zinc particles

A molten mixture of 0.46 g bismuth and 0.50 g zinc (Bi: 48 wt%, 22at%; Zn: 52 wt%, 78 at%) was treated as in the previous cases. The product included some powder together with a solid granule. Examination of a powder sample by SEM (Fig. 13) showed spherical particles, mostly in the micrometric scale, that are partially coated with material of no definite form. EDS elemental analysis of two of the spheres showed almost identical composition; 74 at% Bi : 26 at% Zn. This is very different from the composition of the initial molten mixture, indicating that most of the Zn has not reacted or interacted with the Bi. According to the phase diagram of the Bi-Zn system, the eutectic alloy contains only 6.1 at% Zn. XRD analysis gave separate signals for Bi and Zn (Fig. 13), which means that both metals in this sample retained their crystalline structure.



Fig.12: SEM image of the powder sample that was obtained by sonication of the molten Bi-Zn mixture. EDS analysis was performed on the marked areas, showing an average composition of 74 at% Bi : 26 at% Zn.



Fig. 13: X-ray diffraction obtained from the Bi-Zn particles. Inset: EDS spectrum obtained from this section of the sample. Inset: EDS spectrum obtained from this section of the sample.

This is similar to the case of Bi-Sn, but here the atomic ratio of the metals was far from their eutectic composition and the metals seem to be segregated rather than reside within the same particles. To better examine the nature of this product, a DSC measurement was carried out in the temperature range of 50-600 °C. The need for such high temperature arose from the Bi-Zn phase diagram (Fig. S8), showing that in the range of 37 to 99.3 at% Zn, the melting point of the alloy is higher than that of pure zinc (419.6 °C), reaching 576 °C at ca. 85 at% Zn. Thus, for the composition studied here (77 at% Zn), the expected melting temperature was ca. 560 °C. The DCS measurement was aimed to clarify whether the product was an alloy, exhibiting a single melting signal around 560 °C, or was it a mixture of two solidified metals, exhibiting two separate melting signals. The curve (Fig. S9) includes both separate peaks for Bi (onset temperature 250 °C) and Zn (onset temperature 410 °C), but also a dispersed signal between 510-550 °C. Here, too, the melting temperatures for Bi and Zn were somewhat lower than their regular values due to the small size of the particles. It can be concluded that at this initial composition of the sample, i.e. large atomic excess of Zn, some alloy was formed, which gave rise to the endothermic signal at t>500 °C, whereas the rest of the two metals did not react with each other but rather solidified together, where Zn appears in the SEM images as a coating on the Bi particles.

Discussion

This work examines the interactions between molten bismuth and four other low- m_p metals under ultrasonic irradiation. In all cases micrometric and sub-micrometric particles were formed as a result of the ultrasonic cavitation process in the oil that involves the creation, growth and collapse of gas bubbles. This induces local microjets that apply shear forces on the molten metals and causes their dispersion into particles of spherical shapes, due to the surface tension of the molten metals before they solidify. The types of the resulting products and their elemental compositions were found to be a function of the interacting metals and their relative content in the initial molten mixture. In the cases of Bi-Sn, Bi-Ga and Bi-Zn different kinds of alloys were formed, whereas only In reacted with Bi to form three intermetallic compounds whose proportions were a function of the initial ratio between the interacting metals. The three alloys had heterogeneous compositions of two elemental phases. Each element (but the amorphous Ga) retained its characteristic crystalline structure but the melting points of the alloys were close to those predicted by the phase diagrams, with slight depressions due to the micrometric size of the particles. Table 3 summarizes the types of products of Bi with the four other metals.

<u>Table 3</u>: Summary of the types of products of the interactions between molten bismuth and other molten metals under ultrasonic irradiation

metals	Type of products
Bi - Sn	Two-phase heterogeneous alloy (metal matrix composite).
Bi - In	Bi and In(Bi) phases+Intermetallic compounds: BiIn, Bi ₃ In ₅ , BiIn ₂ .
Bi - Ga	Two-phase mixture: crystalline Bi, amorphous Ga.
Bi - Zn	Heterogeneous alloy, solid mixture.

Two main conclusions can be drawn from the result:

a) The kinds of products of the interaction between each pair of molten metals under ultrasonic irradiation are similar to those obtained under melting without sonication, as reflected in the phase diagrams. The extreme local conditions of pressure and temperature that develop near the surface of the metals by the ultrasonic cavitation (the growth and collapse of gas bubbles in the liquid medium) cannot induce the formation of intermetallic compounds between metals that tend to form alloys.

b) Ultrasonic irradiation of molten mixtures of metals in liquid media is a facile route for preparing alloys in the form of powders, consisted of particles in the micrometric to submicrometric scale.

The first conclusion is not surprising. In a previous work we showed that molten gallium can instantaneously reduce ions of silver, copper or gold in aqueous solutions under ultrasonic irradiation, due to the enormous surface area of the unoxidized gallium particles which are formed. Zinc, however, which has a more negative reduction potential than gallium, cannot be reduced in spite of the extreme local temperatures that develop near the metal surface. The conclusion in this case was that even such extreme conditions could not overcome the energetic barrier associated with reduction of zinc ions by gallium. Here, too, such conditions cannot "force" reactions between metals that normally do not react but rather form alloys.

The second conclusion is important from the applicative perspective, providing a simple method of preparing alloys in the form of particles. A similar method was reported by Han et al. [13] for field's metal, but unlike this case they have started from the molten alloy and used a surfactant.

Conclusions

- 1. Ultrasonic irradiation of the mixtures of molten bismuth with one of the other low m_p metal produced spherical particles in the size-range of sub-micron to several microns in diameters.
- The types of the products are determined by the identity of the interacting metals. For example,
 Bi forms an alloy with Sn and intermetallic compounds with In.
- 3. Bi and In can form three intermetallic compounds: BiIn, Bi_3In_5 and $BiIn_2$. The proportions between them depends on the initial ratio between the metals: when In is in excess, more $BiIn_2$ can be formed.
- Sonication of molten metals of low m_p is a facile method of preparing alloys in the form of micrimetric particles.

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References

[1] R. Ferrando, J. Jellinek, and R. L. Johnston, Chem. Rev. 2008, 108, 845-910.

- [2] J. Luo, L. Wang, D. Mott, P. N. Njoki, N. Kariuki, C. J. Zhong, and T. He, J. Mater. Chem. 2006, 16, 1665-1673.
- [3] C. J. Zhong, J. Luo, P. N. Njoki, D. Mott, B. Wanjala, R. Loukrakpam, S. Lim, L. Wang, B. Fang, and Z. Xu, *Energy Environ. Sci.* 2008, 1, 454-466.
- [4] S.J. Shin, J. Guzman, C.W. Yuan, C. Y. Liao, C.N. Koller, P. R. Stone, O. D. Dubon, A. M. Minor, M. Watanabe, J. W. Beeman, K. M. Yu, J. W. Ager, D. C. Chrzan, and E. E. Haller, *Nano Lett.* 2010, **10**, 2794-2798.
- [5] V. B. Kumar, A. Gedanken, and P. Paik, ChemPhysChem 2013, 14, 3215–3220.
- [6] M. Shintaku, H. Suzuki, K. Kamitsuji, C. Kaito, Jpn. J. Appl. Phys. 2005, 44, 5296.
- [7] E. Sutter, and P. Sutter, *Nano Lett.* 2008, **8**, 411-414.
- [8] E. A. Sutter, and P. W. Sutter, *Nanotechnology* 2011, 22, 295605.
- [9] E. A. Sutter, and P. W. Sutter, ACS Nano 2010, 4, 4943-4947.
- [10] S. Barcikowski, and F. Mafune, J. Phys. Chem. C 2011, 115, 4985-4985.

- [11] H. Zeng, X. W, Du, S. C. Singh, S. A. Kulinich, S. Yang, J. He, W. Cai, Nanomaterials via Laser Ablation/Irradiation in Liquid: A Review, *Adv. Funct. Mater.* 2012, **22**, 1333-1353.
- [12] H. Chen, Z. Li, Z. Wu, and Z. Zhang, J. Alloys and Comp. 2005, 394, 282-285.
- [13] Z. H. Han, B. Yang, Y. Qi, and J. Cumings, Ultrasonics 2011, 51, 485-488.
- [14] H. Friedman, S. Reich, R. Popovitz-Biro, P. von Huth, I. Halevy, Y. Koltypin, A. GedankenZ. Porat, *Ultrasonics Sonochemistry* 2013, 20, 432–444.
- [15] V. B. Kumar, Y. Mastai, Z. Porat, and A. Gedanken, *New J. Chem.*, 2015, DOI: 10.1039/C4NJ02081B.
- [16] V.B. Kumar, A. Gedanken, G. Kimmel, and Z. Porat, *Ultrason. Sonochem.* 2014, 21, 1166-1173.
- [17] V. B. Kumar, Y. Koltypin, A. Gedanken, and Z. Porat, J. Mater. Chem. A, 2014, 2, 1309-1317.
- [18] V. B. Kumar, Z. Porat, G. Kimmel, and A. Gedanken, *J. alloys and comps.* 2015, http://dx.doi.org/10.1016/j.jallcom.2015.02.171
- [19] V. B. Kumar, Z. Porat, and A. Gedanken, J Therm Anal Calorim, 2015, 119, 1587–1592.
- [20] S. L. Lai, J. Y. Guo, V. Petrova, G. Ramanath, and L. H. Allen, *Phys. Rev. Lett.* 1996, 77, 99-102.
- [21] W. T. Nichols, T. Sasaki, and N. Koshizaki, J. Appl. Phys. 2006, 100, 114912-114916.

Table of contents (TOC Graphic)

Formation of bismuth-based binary alloys and intermetallic particles by ultrasonic cavitation

Vijay Bhooshan Kumar¹, Giora Kimmel³, Ze'ev Porat^{2,3*} and Aharon Gedanken^{1,4*}

This work reports the formation of bismuth based alloys. Binary combinations of bismuth and one of other low-melting point metals (Sn, In, Ga and Zn) were melted together in hot silicone oil and irradiated with ultrasonic energy to form micro/nano alloy particles.



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Vijay Bhooshan Kumar¹, Giora Kimmel³, Ze'ev Porat^{2,3*} and Aharon Gedanken^{1,4*}

This work reports an important understanding of the bismuth reactivity with low m_p metals (Sn, In, Ga, Zn).

