Density and ultrasound velocity in Ga-Bi melts

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Abstract. Density $d$ temperature dependences of Ga-Bi melts with 0, 10.2, 16.2, 29.8, 42.0, 51.6, 61.5, 80.0 and 100 at.%Bi were measured using absolute gamma-absorption technique with accuracy of 0.2 to 1.5 % (depending on bismuth concentration). In addition, temperature dependences of ultrasound velocity $υ$ were determined for the samples with 11.0, 16.7, 29.8 and 100 at.% Bi. The accuracy in the acoustic measurements was higher than 0.3%. The special scanning equipment for the gamma-densitometer has allowed to measure density of co-existing phases below the separation cupola. The obtained values coincide with reference data within the declared accuracy. An anomalous behavior of ultrasound velocity (deviation of the $υ(T)$ from linear dependences) and significant increase of ultrasound attenuation were discovered for the samples with 16.7 and 29.8 at.% Bi at the temperatures of 70 to 100 K above the separation cupola. Using the experimental data, the thermal expansion coefficient, molar volume and adiabatic compressibility were calculated. All these characteristics demonstrate linear behavior similar to ideal solutions.

1. Introduction
The alloys with monovariant equilibrium regions are of permanent interest because they are considered to be complicated model systems on one hand and, on the other hand, promising materials for industrial application.

Ga-Bi alloys belong to systems with limited solubility of the components in liquid state. The phase diagram for Ga (99.999 wt.%) – Bi (99.95 wt.%) system was obtained by DTA in [1] for the first time. Binary compounds were not found in this work. The critical point on miscibility curve correspond to 535 K and 30 at.% Bi. At monotectic temperature 495 K the separation of liquids exists at bismuth content from 8.5 to 61.5 at.%. The eutectic point is located at $T = 302.63$ K and bismuth concentration 0.22 at.%. There is no mutual solubility of the components in solid state.

2. Experimental
Density was measured at scanning gamma-densitometer using absolute variant of the method [2]. Ultra sound velocity was obtained by pulse-phase method at the frequency of 31.33 MHz. This method allows to measure ultra sound velocity at different distances from crucible bottom [3] and to determine attenuation coefficient as well.

All the experiments were performed starting from monotectic temperature (495 K) up to 1200 K. The accuracy in density absolute values determination was estimated at a level of 0.2 % for Ga and 1.5 % for Bi. For ultra sound velocity value the accuracy was 0.3 %. The sensitivity was higher than 0.1-0.2 % for both of installations.
3. Result and Discussion

Chemical compositions for the samples and investigated temperature ranges are presented in Table 1.

**Table 1.** Chemical compositions of Ga-Bi melts and investigated temperature intervals $\Delta T$ in density measurements

| N  | Bi, wt.% | Bi, at.% | $\Delta T$, K | Composition, according to [1]                  |
|----|----------|----------|---------------|-----------------------------------------------|
| 1  | 100      | 100      | 545 – 1330    | pure bismuth                                  |
| 2  | 92.30    | 79.99    | 512 – 1370    | intermediate composition                       |
| 3  | 82.71    | 61.47    | 513 – 1280    | monotectic                                    |
| 4  | 76.13    | 51.55    | 528 – 1335    | intermediate composition                       |
| 5  | 68.42    | 41.96    | 536 – 1175    | intermediate composition                       |
| 6  | 55.89    | 29.71    | 532 – 1172    | critical composition                           |
| 7  | 36.62    | 16.16    | 518 – 1172    | intermediate composition                       |
| 8  | 26.51    | 10.74    | 495 – 1153    | intermediate composition                       |
| 9  | 25.46    | 10.23    | 504 – 1154    | intermediate composition                       |
| 10 | 0        | 0        | 303 – 1500    | pure gallium                                  |

**Table 2.** Chemical compositions of Ga-Bi melts and investigated temperature intervals $\Delta T$ in ultra sound velocity measurements

| N  | Bi, wt.% | Bi, at.% | $\Delta T$, K | Composition, according to [1]                  |
|----|----------|----------|---------------|-----------------------------------------------|
| 1  | 100      | 100      | 545 – 1380    | pure bismuth                                  |
| 2  | 55.93    | 29.75    | 536 – 1173    | critical composition                           |
| 3  | 37.45    | 16.65    | 527 – 1268    | intermediate composition                       |
| 4  | 27.03    | 11.00    | 513 – 1274    | intermediate composition                       |
| 5  | 0        | 0        | 350 – 1403    | pure gallium                                  |

Density temperature dependences for investigated Ga-Bi alloys in liquid state are shown in Figure 1. The results for equilibrium states were obtained after samples homogenization. The sample was considered to be homogenized when density values did not depend on vertical axis of the sample and results obtained during heating and subsequent cooling coincide. In order to clarify the pictures, the results obtained during heating and subsequent cooling as well as results of repeated experiments are illustrated by identical symbols. Binodal, liquidus and monotectic lines, obtained from temperatures of anomalies at density curves, are plotted in Figure 1 also.

All the experimental curves can be fitted by linear equation

$$d(T) = d_L \cdot \left[1 - \alpha \cdot (T - T_L)\right],$$

where $T_L$ is a melting point for pure Ga and Bi; or the liquidus temperature for the melt containing 80 at.% Bi; or temperature of monotectic reaction for Ga-61.5 at.% Bi melt; or immiscibility point for all other compositions; $d_L$ density at $T_L$; $\alpha$ – thermal expansion coefficient for the melt.

The values for $d_L$ and $\alpha$ coefficients, obtained by less square method are given in Table 3. $T_L$ values are determined from temperatures of anomalies at density curves.

Ultra sound velocity temperature curves for Ga-Bi melts in the range above miscibility gap are shown in Figure 2. The data for different phases in separated liquid system, obtained in the experiments with Ga – 29.75 at.% Bi and Ga – 16.65 at.% Bi melts, are presented in Figure 2 also. The results of repeated experiments are illustrated by identical symbols. The sizes of the symbols are equal to accidental error range.
**Figure 1.** Density temperature dependences for Ga-Bi melts

**Figure 2.** Ultrasound temperature dependences for Ga-Bi melts. The shift of experimental curves through vertical axis is given in brackets.
Table 3. Approximating coefficient $\alpha$, temperature $T_L$ and density at this temperature $d_L$ for Ga-Bi melts

| Bismuth content, at.% | $d_L$, kg/m$^3$ | $T_L$, K | $\Delta T$, K | $\alpha$, $10^{-4}$ K$^{-1}$ |
|-----------------------|-----------------|----------|--------------|--------------------------|
| 0                     | 6054 ± 5        | 303      | $T_L$ -1500  | 0.999 ± 0.006            |
| 10.23                 | 6658 ± 8        | 512      | $T_L$ -1370  | 1.10 ± 0.01              |
| 10.74                 | 6678 ± 3        | 513      | $T_L$ -1280  | 1.100 ± 0.005            |
| 16.16                 | 6909 ± 6        | 528      | $T_L$ -1335  | 1.050 ± 0.008            |
| 29.70                 | 7738 ± 4        | 536      | $T_L$ -1175  | 1.138 ± 0.005            |
| 41.96                 | 8284 ± 3        | 532      | $T_L$ -1172  | 1.144 ± 0.003            |
| 51.55                 | 8662 ± 2        | 518      | $T_L$ -1172  | 1.190 ± 0.002            |
| 61.47                 | 9018 ± 3        | 496      | $T_L$ -1153  | 1.187 ± 0.003            |
| 79.99                 | 9592 ± 3        | 504      | $T_L$ -1154  | 1.209 ± 0.003            |
| 100                   | 10056 ± 5       | 545      | $T_L$ -1330  | 1.281 ± 0.004            |

The majority of experimental curves can be fitted by linear equation

$$v_S(T) = v_{SL} - \beta \cdot (T - T_L),$$

where $T_L$ is the same, as in (1); $v_{SL}$ - ultra sound velocity at that temperature; $\beta = d v_S / d T$ - ultra sound velocity temperature coefficient. $v_{SL}$ and $\beta$ coefficients obtained by less square method are given in table 4. $T_L$ values were determined either from temperatures of anomalies at ultra sound velocity curves, or using $h(T)$ curve (see [3] for comments).

Table 4. Approximating coefficients and temperature $T_L$ for Ga-Bi melts

| Bismuth content, at.% | $v_{SL}$, m/s | $T_L$, K | $\Delta T$, K | $\beta$, m/(s·K) |
|-----------------------|----------------|----------|--------------|-----------------|
| 100                   | 1645 ± 7       | 545      | $T_L$ -595   | 0.054 ± 0.009   |
|                       | 1641 ± 3 (595K)|         | 595 - 800    | 0.179 ± 0.004   |
|                       | 1604 ± 2 (800K)|         | 800 - 1270   | 0.235 ± 0.002   |
|                       | 1518 ± 6 (1270K)|      | 1270 - 1380  | 0.273 ± 0.004   |
| 29.75                 | 2223 ± 1.5     | 535.5    | 650 - 1173   | 0.287 ± 0.0015  |
| 16.65                 | 2427 ± 4       | 527.5    | 580 - 1268   | 0.289 ± 0.003   |
| 11.00                 | 2541 ± 2       | 513      | 513 - 1274   | 0.277 ± 0.002   |
| 0                     | 2878 ± 2       | 303      | $T_L$ -1270  | 0.300 ± 0.002   |

For Ga – 29.75 at.% Bi and Ga – 16.65 at.% Bi melts the deviations from linear dependence $v=f(T)$ were fixed. They started at 70 and 115 K above critical point respectively (see figure 2). The same effect at concentrations near critical was found in [4,5] earlier. However in some papers the temperature curve $v=f(T)$ [6,7].

In our experiments we determined the attenuation coefficient in the melt with the composition near to critical. The dependence $\alpha/f^2(T)$ vs temperature is given at figure 3. In spite of rather big uncertainties in experimental values, the significant increase of attenuation coefficient at 50 K before separation temperature was found during cooling. This result is in good agreement with the data given in [6].

The concentration dependences for density $d$, thermal expansion coefficient $\alpha$ and molar volume $V$ for Ga-Bi melts at 873 K are presented in figures 4-6. For comparison, the results from [6] are given in these figures also. One can see that good agreement of our results with data from [6] is obtained for pure Ga and Bi only. For the other compositions our results are higher. It may be connected with rather low activity of gamma-rays source used in [6] and, subsequently, rather big accidental error in that work.
The concentration curve of thermal expansion coefficient (see figure 5) can be fitted with good accuracy by linear function
\[ \alpha(x) = -[(2.34 \pm 0.29) \cdot 10^{-7} \cdot x + (1.045 \pm 0.015) \cdot 10^{-4}], \]
where \( x \) – bismuth content, at.%.

The molar volume isotherm looks like straight line in the frames of mentioned error bars (figure 6). Let us note, that the small positive deviation from ideal dependence was fixed in [6].

In figure 7, the 541.4 K – isotherm of sound velocity is plotted by the linear approximation (2) of experimental data, in comparison with the results presented in literature. One can see the coincidence of our investigation results with those of high-frequency (>10 MHz) experiments [6,7]. In [6], the accuracy was declared as 0.7 %, and in [7] as 0.1%. Within the frames of the accuracy, the data obtained may be fitted by Kudryavtsev equation
\[ \nu_s^2 = \sum_{i=1}^{n} x_i \nu_{si}^2, \]
where \( \nu_s \) is the mixture sound velocity, \( \nu_{si} \) is the sound velocity in the \( i \)-th component, and \( x \) is the component mass fraction.

The literature, data on sound velocity are rather detailed, and found to be in a good agreement with our measurements in the two-phase area also.

On figure 8, concentration dependency of Ga-Bi melts adiabatic compressibility at 573 K is shown. The compressibility was calculated as
\[ \beta_s = (d^{-1} \cdot \nu_s^2)^{-1}. \]

Figure 3. The temperature dependency of attenuation coefficient near the critical concentration at 31.33 MHz (● – cooling).

Figure 4. Density isotherm of Ga-Bi melts at 873 K. ● – this work; ○ – [6].

Figure 5. Thermal expansion coefficient isotherm for Ga-Bi melts at 873 K. ● – this work, ○ – [6], the lines correspond to the linear approximation.

Figure 6. Molar volume isotherm for Ga-Bi melts at 873 K. ● – this work; ○ – [6].
For comparison, the adiabatic compressibility temperature dependency for an ideal mixture $\beta_{S_{id}}$, :

$$\beta_{S_{id}} = \frac{\left[(1-x)V_{Ga}\beta_{Ga} + xV_{Bi}\beta_{Bi}\right]}{V_{id}},$$  \hspace{1cm} (4)

is also shown. Here, lower index denotes the components, $V$ and $\beta$ are the molar volume and compressibility respectively, and $V_{id}$ is the molar volume of ideal mixture Ga$_{1-x}$Bi$_x$. One can see that $\beta_S$ differs from $\beta_{S_{id}}$. Small negative deviations were also found by other researches.

![Figure 7](image1.png)  \hspace{1cm} ![Figure 8](image2.png)

**Figure 7.** Ultrasound velocity isotherm for Ga-Bi melts at 541.4 K. ● – this work; ○ – [7]; △ – [6]; ▲ – [5]; ♦ – [8]. Solid line corresponds to the Kudryavtcev equation.

**Figure 8.** Adiabatic compressibility isotherm for Ga-Bi melts at 573 K. ● – this work; ○ – [7], △ – [6]. Solid line corresponds to ideal isotherm.

### 4. Conclusions

Density and sound velocity absolute values are in coincidence within the accuracy frames with those presented in literature [6, 7]. In the present work, the temperature region of measurements has been essentially expanded, and the accuracy of above values determination has been enhanced. The sound velocity was measured in co-existing phases in a wide temperature range. Novel reliable data on densities of co-existing phases was obtained due to the possibility of measurements along vertical axis.

On the base of data obtained, the adiabatic compressibility temperature curves were calculated. Near the immiscibility temperature, anomalous behavior of single-phase melts was found at 16.65 and 29.75 at% Bi. Also, an essential rise of sound dumping was found near the critical point.

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