Thermodynamic Properties of Barium-Bismuth Alloys Determined by Emf Measurements

Timothy Lichtenstein¹, Nathan Smith¹, Jarrod Gesualdi¹, Kuldeep Kumar¹, Hojong Kim^{1*}

¹Materials Science and Engineering, The Pennsylvania State University, 406 Steidle Building,
University Park, PA 16802, United States

Corresponding Author:

*E-mail: huk29@psu.edu. Tel: 814-865-3117. Fax: 814-865-2917

KEYWORDS: Barium-Bismuth alloys, Emf method, Thermodynamic properties, Barium-Bismuth phase diagram

ABSTRACT

Thermodynamic properties of Ba-Bi alloys, including the activity, partial molar entropy and enthalpy, were determined using the electromotive force (emf) technique for fourteen compositions, $x_{\text{Ba}} = 0.05\text{--}0.80$. Emf measurements were performed at ambient pressure using a Ba(s)|CaF₂-BaF₂|Ba(in Bi) or Ba-Bi($x_{\text{Ba}} = 0.05$)|CaF₂-BaF₂|Ba(in Bi) electrochemical cells at 723–1073 K. At 773K, activity values of Ba were as low as 6.6×10^{-16} at mole fraction $x_{\text{Ba}} = 0.05$ and approached unity for mole fractions $x_{\text{Ba}} \geq 0.80$. Stable emf values were observed at mole fractions $x_{\text{Ba}} = 0.05\text{--}0.25$, exhibiting less than a 5 mV difference between the heating and cooling cycles. Mole fractions $x_{\text{Ba}} \geq 0.30$ exhibited increased hysteresis or had an unexpected emf profile due to the formation of metastable phases such as Bi and Ba₅Bi₃, confirmed by X-ray diffraction. The Ba-Bi alloys were further characterized using differential scanning calorimetry over the entire composition range. Based on these data, a revised Ba-Bi binary phase diagram is proposed.

1. INTRODUCTION

Thermochemical properties of binary Ba-Bi alloys were investigated using the electromotive force (emf) technique to assess the viability of Bi electrodes in separating Ba species from molten salt electrolytes. Recently, Kim *et al.* investigated the electrochemical properties of bismuth electrodes in a BaCl₂-LiCl-CaCl₂-NaCl (16-29-35-20 mol%) electrolyte at 773–973 K. They identified Ba to be preferentially deposited over Na, Ca or Li due to Ba having the strongest atomic interactions with Bi, i.e. the lowest thermodynamic activity values of Ba in the Bi metal among alkali/alkaline-earth constituents [1,2].

Delcet *et al.* determined the thermodynamic properties of Ba-Bi alloys up to $x_{\text{Ba}} = 0.50$ by coulometric titration using a single-crystal BaF₂ electrolyte at 1123 K. The activity values of Ba in Bi were as low as 2×10^{-12} at $x_{\text{Ba}} = 0.05$; however, they reported that the results were not accurate due to uncertainty in Ba compositions (up to 3 mol%) during the coulometric titration [3]. Pure Ba metal is highly reactive and well known to have a high solubility in its own halide salts (e.g., ~15 mol% in BaCl₂ at 1163 K) [4]; barium metal dissolved in the halide electrolyte can promote electronic conduction through the electrolyte and prevent accurate compositional accounting by coulometric titration using halide electrolytes.

In this work, a solid-state binary CaF₂-BaF₂ (97-3 mol%) electrolyte was employed to determine the emf values of Ba-Bi alloys at fixed compositions over 723–1073 K. In the binary CaF₂-BaF₂ system, CaF₂ is more stable than BaF₂ due to having a more negative potential versus the F⁻/F₂ redox couple, implying barium ions are the more electroactive species in the CaF₂-BaF₂ electrolyte. For example, at 800 K the standard electrode potential is –5.65 V for Ca²⁺/Ca and –5.58 V for Ba²⁺/Ba, calculated using the Nernst equation and the standard free energies of formation for CaF₂ and BaF₂ [5]. Utilizing the relatively high ionic conductivity of CaF₂ ($\sim 1.5 \times$

$10^{-3} \text{ S cm}^{-1}$ at 1073 K) [6] and higher stability than pure BaF_2 , the binary $\text{CaF}_2\text{-BaF}_2$ electrolyte will allow for accurate emf measurements of Ba-Bi alloys using the electrochemical cell:

where pure Ba is the reference electrode (RE), solid $\text{CaF}_2\text{-BaF}_2$ is the electrolyte, and Ba-Bi alloys are the working electrodes (WE). Considering that $\text{CaF}_2\text{-BaF}_2$ is a fluoride-ion conducting electrolyte [6], the half-cell reactions are

and the overall cell reaction is

For this cell reaction, the change in partial molar Gibbs free energy of barium, $\Delta\bar{G}_{\text{Ba}}$, is given by:

$$\Delta\bar{G}_{\text{Ba}} = \bar{G}_{\text{Ba(in Bi)}} - G_{\text{Ba(s)}}^0 = RT \ln a_{\text{Ba(in Bi)}} \quad (5)$$

where $\bar{G}_{\text{Ba(in Bi)}}$ is the partial molar Gibbs free energy of barium in bismuth, $G_{\text{Ba(s)}}^0$ is the standard Gibbs free energy of pure barium, R is the ideal gas constant, T is the temperature, and $a_{\text{Ba(in Bi)}}$ is the activity of barium in bismuth, referred to as a_{Ba} moving forward. By applying the Nernst equation ($\Delta\bar{G}_{\text{Ba}} = -zFE_{\text{cell}}$) to equation (5), the measured cell emf, E_{cell} , is related to the change in partial molar Gibbs free energy of barium by

$$E_{\text{cell}} = -\frac{\Delta\bar{G}_{\text{Ba}}}{zF} = -\frac{RT}{zF} \ln a_{\text{Ba}} \quad (6)$$

where F is the Faraday constant and z is the number of electrons exchanged in the half-cell reactions ($z = 2$).

Due to the high reactivity of pure Ba metal leading to the rapid degradation electrolyte during emf measurements at elevated temperatures, we used a less reactive Ba-Bi alloy at $x_{\text{Ba}} = 0.05$ as the reference electrode for emf measurements of Ba-Bi alloys $x_{\text{Ba}} = 0.10\text{--}0.80$, using the following cell:

where the reference electrode is denoted as underlined. The cell potential E_{I} of this electrochemical cell is

$$E_{\text{I}} = -\frac{RT}{2F} \ln \left(\frac{a_{\text{Ba}}}{a_{\text{Ba}}^*} \right) \quad (8)$$

where a_{Ba}^* is the activity at mole fraction $x_{\text{Ba}} = 0.05$.

In separate experiments, the electrode potential of the Ba-Bi alloy at $x_{\text{Ba}} = 0.05$ was determined against pure Ba, using the following cell:

where the cell potential E_{II} is

$$E_{\text{II}} = -\frac{RT}{2F} \ln a_{\text{Ba}}^* \quad (10)$$

Then, the summation of these two cell potentials ($E_{\text{I}} + E_{\text{II}}$) results in the cell potential (E_{cell}) of Ba-Bi alloys relative to pure Ba according to:

$$E_{\text{cell}} = E_{\text{I}} + E_{\text{II}} = -\frac{RT}{2F} \ln a_{\text{Ba}} \quad (11)$$

In analyzing the thermodynamic properties of Ba-Bi alloys, emf measurements were corroborated using powder X-ray diffraction (XRD) and differential scanning calorimetry (DSC) to determine the relevant crystal structures and phase transition temperatures for each alloy

composition. These data were used to construct a revised Ba-Bi phase diagram over the full composition range, which includes the new phases of $\text{Ba}_{11}\text{Bi}_{10}$, Ba_4Bi_3 , and Ba_2Bi .

2. EXPERIMENTAL

2.1 Fabrication and assembly of electrochemical cell components

Synthesis of CaF_2 - BaF_2 electrolyte: Binary CaF_2 - BaF_2 (97-3 mol%) electrolyte for emf measurements was prepared by mixing the appropriate amounts of BaF_2 (99.999%, Sigma Aldrich, Stock No. 652458) and CaF_2 (99.5%, Alfa Aesar, Stock No. 11055) powders. Approximately 500 g of the binary mixture was added with 40 g of polyvinyl alcohol as binder, 20 g of polyethylene glycol plasticizer, and 1 L of isopropyl alcohol. The mixture was ball-milled using yttria-stabilized zirconia media (3 mm diameter, TOSOH USA) for 24 h and then dried in air.

About 130 g of the ball-milled, dry powder was uniaxially pressed at 30 MPa into a green pellet (75 mm diameter and 17 mm thickness). Seven wells (each with 11.2 mm diameter and 12 mm depth) were drilled into the green pellet: one in the center for a thermocouple and six wells for Ba-Bi alloy electrodes evenly spaced about 25.4 mm from the center (Figure 1). The green pellet was heated in a box furnace in air at 393 K for 12 h at 5 K min^{-1} to remove moisture, at 823 K for 12 h at 2.5 K min^{-1} to burn out organic binder and plasticizer, and at 1273 K for 3 h at 5 K min^{-1} to sinter. Similarly, electrolyte caps were fabricated from ~4 g of the mixture (19 mm diameter and 10 mm height) with a 1 mm center hole and sintered. During the final cell assembly, these electrolyte caps were placed on top of the electrode wells to minimize the cross contamination between the electrodes through vapor-phase transport at elevated temperatures.

[Figure 1]

Fabrication of Ba-Bi alloy electrodes: Ba-Bi alloys were fabricated using a laboratory arc-melter (MAM1, Edmund Bühler GmbH). Barium (99.2%, Alfa Aesar, Stock No. 00653) and bismuth (99.999%, Sigma Aldrich, Stock No. 556130) pieces were weighed in appropriate quantities in an argon-filled glovebox ($O_2 < 0.5$ ppm and $H_2O < 1.5$ ppm) and arc-melted together under an inert argon atmosphere. Ba-Bi alloys were machined into cylindrical shapes with approximate dimensions of 10 mm diameter and 7 mm height with a ~2 mm center hole to insert a tungsten electrical lead during electrochemical cell assembly. At the beginning of emf measurements, the cell assembly was held at 1073 K to melt alloy electrodes and to establish stable physical contact with the electrolyte and the tungsten electrical lead.

Ba-Bi alloys at mole fractions $x_{Ba} = 0.45$ – 0.55 were too brittle to fabricate in a cylindrical shape and stable electrical contact was difficult to establish due to their high melting temperatures (> 1043 K). Instead, these alloys were induction melted on top of a boron nitride plate using an induction heater (IH15A-2T, Across International), custom-installed inside the glovebox. In this case, the tungsten electrical lead was immersed into the molten metal pool, and then the alloys were cooled while maintaining electrical contact with the tungsten wire. Similarly, electrical contact between the pure barium metal and the tungsten lead wire was established using the induction heater due to the high reactivity of molten Ba with the electrolyte.

Electrochemical cell assembly: The electrochemical cell (Figure 1) was assembled inside an argon-filled glovebox to minimize reaction of the electrodes with oxygen and moisture. The synthesized CaF_2 - BaF_2 electrolyte was placed in an alumina crucible (8.2 cm diameter and 3.0 cm height, AdValue Technology, Stock No. AL-4120) with the alloy electrodes in the electrolyte wells, and tungsten electrical leads (1mm diameter and 46 cm length) inserted through the stainless steel test chamber, through insulating alumina sheaths, through the electrolyte caps, and

1
2
3
4 into the Ba-Bi alloy electrodes. The test chamber was sealed inside the glovebox, removed from
5
6 the glovebox, and transferred into a crucible furnace.
7
8

9 **2.2 Emf measurements**

10
11 For electrochemical measurements, the test chamber was evacuated to less than 0.7 Pa,
12
13 heated at 373 K for 10 h and at 543 K for 10 h to remove residual moisture, purged with ultra
14
15 high-purity argon gas three times, and then heated to 1073 K under a slow flow of argon (~10
16
17 mL min⁻¹) to melt the electrodes and establish electrical contact between cell components. The
18
19 cell temperature was recorded using an ASTM K-type thermocouple and a thermocouple data
20
21 acquisition system (NI 9211, National Instruments).
22
23

24
25
26 Emf measurements, using Ba-Bi alloy reference electrode at $x_{\text{Ba}} = 0.05$ (cell type I), were
27
28 performed continuously while cooling from 1073 K down to 723 K and heating back to 1073 K.
29
30 During the thermal cycle, the cell temperature was held constant for 1.5 h in 25 K steps to reach
31
32 thermal equilibrium. In the calibration experiments using the pure Ba reference electrode (cell
33
34 type II), the cell temperatures were maintained below 973 K due to rapid degradation of the
35
36 electrochemical cells above the melting temperature of barium ($T_{\text{m, Ba}} = 1000$ K). The emf values
37
38 between the working and reference electrodes were continuously measured using a potentiostat-
39
40 galvanostat (Autolab PGSTAT302N, Metrohm AG) for 180 s sequentially among Ba-Bi alloy
41
42 WEs.
43
44
45
46
47

48 For cell type I, the potential difference between the two identical REs ($x_{\text{Ba}} = 0.05$) was
49
50 less than 2 mV over the entire thermal cycle. For the cell type II, the potential difference between
51
52 the pure barium REs drifted and diverged over time due to the high reactivity of pure Ba. In cell
53
54 type II, the emf values of Ba-Bi alloy at $x_{\text{Ba}} = 0.05$ were taken only when the potential difference
55
56 between the pure barium REs was less than 5 mV for better precision.
57
58
59
60
61
62
63
64
65

2.3 Characterization of Ba-Bi alloys

Phase analysis: Phase characterization was performed by powder X-ray diffraction using an X-ray diffractometer (XRD, PANalytical Empyrean) over 2θ angles 20–75°. The alloy samples were ground into a fine powder in an argon-filled glovebox using a mortar and pestle, and the powder samples were coated with mineral oil to minimize oxidation during measurements. The presence of mineral oil resulted in a broad amorphous background spectrum at low angles ($2\theta < 30^\circ$), and the background was subtracted for phase analysis.

Thermal analysis: Differential scanning calorimetry (DSC) was performed using a thermal analyzer (Netzsch, STA 449 F3 Jupiter). About 20–50 mg of each arc-melted alloy ($x_{\text{Ba}} = 0.05\text{--}0.95$) was placed on tungsten foil inside an alumina sample crucible to prevent a direct reaction between the Ba-Bi alloy and alumina. Thermograms were collected during heating-cooling cycles at multiple scan rates of 5–20 K min^{−1} under high-purity argon flow (100 mL min^{−1}). The phase transition temperatures were determined from the onset temperatures at various scan rates by extrapolating the onset temperatures to 0 K min^{−1} [7].

3. RESULTS AND DISCUSSION

3.1 Emf measurements

Figure 2a displays the measured emf values, E_{I} , of Ba-Bi alloys ($x_{\text{Ba}} = 0.05, 0.10, 0.20$) and cell temperature as a function of time, using a Ba-Bi($x_{\text{Ba}} = 0.05$)|CaF₂-BaF₂|Ba(in Bi) cell. The potential difference between the two identical Ba-Bi alloys at $x_{\text{Ba}} = 0.05$ was less than 2 mV during the entire measurement. Moreover, a symmetric emf profile during the heating and cooling cycles indicates that the emf measurements were reproducible, in particular at low Ba compositions. In general, the use of the less reactive Ba-Bi alloy RE enabled highly reproducible

emf measurements (E_I) of Ba-Bi alloys over a wide range of mole fractions $x_{Ba} = 0.10$ – 0.80 at 723 – 1073 K.

[Figure 2]

In separate experiments, a $Ba(s)|CaF_2-BaF_2|Ba-Bi(x_{Ba} = 0.05)$ cell was employed to determine the emf values of Ba-Bi alloy at $x_{Ba} = 0.05$ relative to pure barium, E_{II} (Figure 2b).

The emf values were linear as a function of temperature according to:

$$E_{II} = 1.97 \times 10^{-4} T + 1.011 \text{ [V]}. \quad (12)$$

Using the linear equation (12), emf values of Ba-Bi alloys were reported against pure barium as

$$E_{cell} (= E_I + E_{II}).$$

Figure 3 displays the variation of emf values with respect to temperature for Ba-Bi alloys $x_{Ba} = 0.05$ – 0.80 . In Figure 3a, above the liquidus [liquid = liquid + $BaBi_3$], the emf increases linearly as temperature increases, and decreases monotonically as x_{Ba} increases. Below the liquidus, for Ba-Bi alloys up to $x_{Ba} = 0.25$, emf values converge onto a single line because the activity of barium is invariant with composition in this two-phase region [liquid + $BaBi_3$]. Mole fraction $x_{Ba} = 0.30$ exhibited a liquidus [liquid = liquid + $BaBi_3$] transition at ~ 874 K and is expected to undergo solidus transition [liquid + $BaBi_3 = BaBi_3 + Ba_{11}Bi_{10}$] based on our revised phase diagram (section 3.4); however, the emf values exhibited a discontinuity at ~ 812 – 836 K and collapsed onto the line defined as liquid + $BaBi_3$, possibly due to the formation of non-equilibrium Bi phase during the solidification.

[Figure 3]

In Figure 3b, $x_{Ba} = 0.40$ exhibited two transition temperatures of liquidus [liquid = liquid + $Ba_{11}Bi_{10}$] at ~ 910 K and solidus [liquid + $Ba_{11}Bi_{10} = Ba_{11}Bi_{10} + BaBi_3$] at ~ 837 K. Interestingly, mole fraction $x_{Ba} = 0.35$ exhibited a direct eutectic transition [liquid = $Ba_{11}Bi_{10} +$

BaBi₃] at ~843 K. Below this solidus (or eutectic) transition temperature, emf values of these two compositions converged together within 10 mV difference. Mole fractions $x_{\text{Ba}} = 0.45\text{--}0.55$ exhibited increased hysteresis during a cooling-heating cycle, up to 20 mV difference, possibly due to the increased reactivity at high Ba concentrations and/or unstable physical contact between the solid-state alloy WE and the electrolyte. In the composition range of $x_{\text{Ba}} = 0.45\text{--}0.55$, emf values during heating cycles exhibited a reproducible linear behavior and were therefore included in the analysis. As expected, a rapid drop in emf values was observed at high Ba mole fractions $x_{\text{Ba}} = 0.75\text{--}0.80$ (Figure 3c) as the alloy composition approached pure Ba ($a_{\text{Ba}} = 1$).

From the linear fits of the data presented in Figure 3, the change in partial molar entropy of Ba in Bi, $\Delta\bar{S}_{\text{Ba}}$, was calculated from the thermodynamic relation:

$$\Delta\bar{S}_{\text{Ba}} = - \left(\frac{\partial \Delta\bar{G}_{\text{Ba}}}{\partial T} \right)_P = 2F \left(\frac{\partial E_{\text{cell}}}{\partial T} \right)_P \quad (13)$$

and the change in partial molar enthalpy $\Delta\bar{H}_{\text{Ba}}$ was obtained from the Gibbs-Helmholtz relation:

$$\Delta\bar{H}_{\text{Ba}} = -T^2 \left(\frac{\partial(\Delta\bar{G}_{\text{Ba}}/T)}{\partial T} \right)_P = 2FT^2 \left(\frac{\partial(E_{\text{cell}}/T)}{\partial T} \right)_P \quad (14)$$

and the results are summarized in Table 1. The change in partial molar entropy and enthalpy were assumed to be temperature independent over the fitted range.

[Table 1]

The activity of Ba was determined using the emf values and the Nernst equation at 773 K, 873 K, and 973 K:

$$\ln a_{\text{Ba}} = -\frac{2F}{RT} E_{\text{cell}} \quad (15)$$

The excess partial molar Gibbs free energy $\overline{G}_{\text{Ba}}^{\text{E}}$ was also calculated using

$$\overline{G}_{\text{Ba}}^{\text{E}} = RT(\ln a_{\text{Ba}} - \ln x_{\text{Ba}}) = RT \ln \gamma_{\text{Ba}} \quad (16)$$

where γ_{Ba} is the activity coefficient of Ba. The emf values, natural log of the activity, and the excess partial molar Gibbs free energy are summarized in Table 2 at each temperature. Figure 4 displays these thermodynamic properties as a function of mole fraction at 773 K, including the liquidus composition estimated by emf measurements and intermetallic compounds determined by XRD in this study (Section 3.2).

[Table 2]

[Figure 4]

Based on equilibrium thermodynamics at a given temperature, the emf values will decrease in the single-phase region as x_{Ba} increases and remain constant in the two-phase regions, according to the Gibbs phase rule. This equilibrium behavior was well observed at $x_{\text{Ba}} = 0.05\text{--}0.25$, as can be seen in Figure 4a where the emf values monotonically decreases as x_{Ba} increases in the liquid phase ($x_{\text{Ba}} \leq 0.18$) at 773K. In the two-phase [liquid + BaBi_3] region ($0.18 < x_{\text{Ba}} < 0.25$), the emf values were nearly constant at 1.08 V, and thus the activity values (Figure 4b). At low Ba mole fractions, a large excess partial molar Gibbs free energy was observed, as low as -205 kJ mol^{-1} , due to strong chemical interactions between Ba and Bi (Figure 4c). However, in the two-phase regions [$\text{BaBi}_3 + \text{Ba}_{11}\text{Bi}_{10}$] and [$\text{Ba}_2\text{Bi} + \text{Ba}$], the emf values continued to decrease as x_{Ba} increased (Figure 4a), deviating from equilibrium phase behavior. Such a deviation was found to originate from the presence of non-equilibrium phases within these composition ranges, confirmed by XRD analysis (see section 3.2).

Using the linear fits of emf values in the liquid phase, the emf values of selected mole fractions $x_{\text{Ba}} = 0.05\text{--}0.20$ were extrapolated at 1123 K and compared to the results by Delcet *et*

al. (Table 3). In general, the difference in emf values at each composition were within 30–70 mV, however, the emf values from this study were consistently lower compared to the values obtained by Delcet *et al* [3]. The difference can be attributed to, in part, the uncertainty in compositional accounting of Ba in their coulombic titration due to increased electronic conductivity at elevated temperatures.

[Table 3]

3.2 Phase analysis of Ba-Bi alloys by XRD

Powder X-ray diffraction data were collected on each arc-melted Ba-Bi alloy and the representative XRD patterns are shown in Figure 5. The measured diffraction patterns were analyzed based upon the reported crystal structures in the Ba-Bi system, listed in Table 4 [8–14]. At mole fractions $x_{\text{Ba}} = 0.05\text{--}0.25$, only two equilibrium phases of Bi and BaBi_3 were observed, supporting the equilibrium behavior of the emf (or activity) trends found in this composition range (Figure 3a and Figure 4a-b). However, at mole fractions $x_{\text{Ba}} > 0.25$, the presence of non-equilibrium phases was apparent, including metastable Bi phase at $x_{\text{Ba}} = 0.30\text{--}0.50$ and Ba_5Bi_3 phase at $x_{\text{Ba}} = 0.70$. The presence of non-equilibrium phases during emf measurements will incur increased cell emf from equilibrium value depending upon the degree of meta-stability, leading to an erratic emf profile.

[Table 4]

[Figure 5]

At mole fractions $x_{\text{Ba}} = 0.25\text{--}0.52$, two-phase $[\text{BaBi}_3 + \text{Ba}_{11}\text{Bi}_{10}]$ equilibrium is expected, however, the presence of metastable Bi phase was clearly observed (Figure 5a). Mole fraction $x_{\text{Ba}} = 0.30$ deviated from this equilibrium behavior and was primarily comprised of Bi and BaBi_3 , which may explain why emf values converged toward [liquid + BaBi_3] line below ~ 812 K

(Figure 3a). Interestingly, mole fractions $x_{\text{Ba}} = 0.45$ and 0.50 were comprised of three phases: BaBi_3 , $\text{Ba}_{11}\text{Bi}_{10}$, and metastable Bi (Figure 5a). As exemplified in Figure 4a at 773 K , the inconsistent emf values over $x_{\text{Ba}} = 0.25\text{--}0.52$ were attributed to the presence of metastable Bi phase.

Similarly, at mole fractions $x_{\text{Ba}} > 0.67$, two-phase $[\text{Ba}_2\text{Bi} + \text{Ba}]$ equilibrium is expected, and we anticipate that the emf values at fixed temperature will approach zero due to the presence of pure Ba phase, as observed in the Ca-Bi system [15]. However, the pure Ba phase was absent from mole fraction $x_{\text{Ba}} = 0.70$, and was identified only at a higher Ba mole fraction $x_{\text{Ba}} = 0.90$. Interestingly, mole fraction $x_{\text{Ba}} = 0.70$ was primarily composed of Ba_2Bi and metastable Ba_5Bi_3 (Figure 5b). The non-equilibrium phase behavior found at $x_{\text{Ba}} = 0.70$ explains an exceptionally high emf value of $\sim 0.65\text{ V}$ at 773 K and their subsequent rapid decrease at higher Ba mole fractions (Figure 4a).

3.3 Thermal analysis

Phase transition temperatures of Ba-Bi alloys $x_{\text{Ba}} = 0.05\text{--}0.95$ were investigated using DSC at multiple scan rates of $5\text{--}20\text{ K min}^{-1}$. Representative DSC scans collected upon heating and cooling of Ba-Bi alloys at 20 K min^{-1} are shown in Figure 6, in which major phase transitions are designated by roman numerals (I-V). The transition temperatures were determined based on linear fits of onset temperatures as a function of scan rate and extrapolating to 0 K min^{-1} . The results are summarized in Table 5. In DSC measurements, the presence of metastable bismuth phase was also apparent at compositions up to $x_{\text{Ba}} = 0.35$. Imprecision in DSC measurements was observed for Ba-Bi alloys, especially at high temperatures and high Ba compositions, and was likely due to the high reactivity of Ba-Bi alloys at elevated temperatures and the formation of non-equilibrium phases at tested heating/cooling rates.

[Figure 6]

[Table 5]

3.4 Phase diagram

Based upon phase transition temperatures from emf and DSC measurements and crystal structures from XRD analysis, a revised Ba-Bi phase is proposed in Figure 7. The transition temperatures by emf results were obtained from the intersection of the linear fits to the emf data as a function of temperature at each mole fraction. Based on the phase behavior from the revised phase diagram, reactions were assigned to the measured transition temperatures (I-V) in Table 6 in comparison with the previous work. In general, the transition temperatures from two separate techniques of DSC and emf measurement, agreed within 10 K difference.

The most recent Ba-Bi phase diagram was reported by Okamoto [16] who primarily used the differential thermal analysis data reported by Grube and Dietrich up to $x_{\text{Ba}} = 0.30$ [17]. In this composition range, they reported eutectic transition reaction [I: liquid = Bi + BaBi₃] at 535 K, in good agreement with this study at 537 K. They also reported an undefined peritectic reaction [liquid + unknown phase = BaBi₃] at 720 K over $x_{\text{Ba}} = 0.24$ –0.30, which was not identified in this study. Instead, this study suggests that the eutectic reaction [II: liquid = BaBi₃ + Ba₁₁Bi₁₀] at ~846 K is the most probable transition reaction in this composition range.

Additional transition reactions and temperatures were also observed at high Ba mole fractions. Mole fractions $x_{\text{Ba}} = 0.55$ and 0.60 exhibited a transition temperature at ~1007 K across the Ba₄Bi₃ ($x_{\text{Ba}} = 0.57$) phase, which is thought to be the allotropic transition reaction [III: Ba₄Bi₃ (rt) = Ba₄Bi₃ (ht)]. The eutectic transition reaction [IV: liquid = Ba₂Bi + Ba(ht)] was observed from both DSC and emf measurements at ~864–873 K, and the allotropic reaction [V: Ba (rt) = Ba (ht)] at 796 K from DSC measurement.

Not included in this phase diagram are the crystalline phases of $\text{Ba}_{16}\text{Ba}_{11}$ and Ba_2Bi_3 . Ponou *et al.* reported that a single crystal Ba_2Bi_3 phase was obtained through a reaction at 1123 K in a sealed Nb crucible, followed by annealing at 773 K for 48 h with slow cooling rate 1 K min^{-1} [18]; Leon-Escamilla *et al.* obtained $\text{Ba}_{16}\text{Bi}_{11}$ through a reaction at 1273 K in a Ta crucible, followed by annealing at 1098–1173 K for 8–24 h [19]. However, these two phases were not observed in this study, possibly due to relatively high heating-cooling rates ($> 5 \text{ K min}^{-1}$) in DSC measurements and insufficient time (1.5 h) for reaching equilibrium in emf measurements.

[Table 6]

[Figure 7]

4. CONCLUSIONS

Thermodynamic properties of binary Ba-Bi alloys were determined by emf, DSC, and XRD techniques. These measurements determined the activity, partial molar entropy, enthalpy, transition temperatures, as well as transition reactions of Ba-Bi alloys, resulting in a revised Ba-Bi phase diagram. Near equilibrium phase behavior was observed at $x_{\text{Ba}} = 0.05\text{--}0.25$, resulting in reliable emf measurements while erratic emf behavior was observed at higher Ba mole fractions due to the formation of metastable phases.

The revised phase diagram suggests that liquid-state solubility of Ba in Bi is ~18 mol% at 773 K and increases up to ~40 mol% at 923 K. The activity values of Ba were as low as $\sim 10^{-15}$ at $x_{\text{Ba}} = 0.05$ and 773 K, implying strong chemical interactions between Ba and Bi. Based upon such a low thermodynamic activity and high liquid-state solubility, liquid Bi metal shows promise as an electrode material in separating Ba ions from molten salt electrolytes (e.g., LiCl-KCl-BaCl_2).

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16 **Acknowledgements:**
17

18
19 The financial support of the US Department of Energy, Office of Nuclear Energy's Nuclear
20 Energy University Programs (Award No. DE-NE0008425) is gratefully acknowledged. The
21 authors would like to thank Tobias Frueh for his advice in synthesizing the solid electrolyte
22 using powder processing techniques, Michael Brova for helpful discussion with thermal analysis,
23 and Jason Munro for his help in processing a large amount of data.
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

References:

- [1] H. Kim, N. Smith, K. Kumar, T. Lichtenstein, Electrochemical Separation of Barium into Liquid Bismuth by Controlling Deposition Potentials, *Electrochim. Acta.* 220 (2016) 237–244. doi:10.1016/j.electacta.2016.10.083.
- [2] H. Kim, D.A. Boysen, T. Ouchi, D.R. Sadoway, Calcium-bismuth electrodes for large-scale energy storage (liquid metal batteries), *J. Power Sources.* 241 (2013) 239–248. doi:10.1016/j.jpowsour.2013.04.052.
- [3] J. Delcet, A. Delgado-Brune, J.J. Egan, Coulometric Titrations Using CaF₂ and BaF₂ Solid Electrolytes to Study Alloy Phases, in: Y.A. Chang, J.F. Smith (Eds.), *Symp. Calc. Phase Diagrams Thermochemistry Alloy Phases*, Metallurgical Society of AIME, Milwaukee, 1979: pp. 275–287.
- [4] H. Schäfer, A. Niklas, Sudwestdeutsche Dozententagung in Freiburg/Br., *Angew. Chemie.* 64 (1952) 611.
- [5] HSC Chemistry 5.1, F. Outokumpu Research Oy, Finland, 2002.
- [6] R.W. Ure, Ionic Conductivity of Calcium Fluoride Crystals, *J. Chem. Phys.* 26 (1957) 1363–1373. doi:10.1063/1.1743547.
- [7] E.B. Ferreira, M.L. Lima, E.D. Zanotto, DSC method for determining the liquidus temperature of glass-forming systems, *J. Am. Ceram. Soc.* 93 (2010) 3757–3763. doi:10.1111/j.1551-2916.2010.03976.x.
- [8] M.E. Straumanis, The precision determination of lattice constants by the powder and rotating crystal methods and applications, *J. Appl. Phys.* 20 (1949) 726–734.

- doi:10.1063/1.1698520.
- [9] N.N. Zhuravlev, V.R. Adamyan Melik, Study of the crystal structure of the superconducting compounds SrBi₃ and BaBi₃, Sov. Phys. Crystallogr. 6 (1961) 99–100.
- [10] G. Derrien, M. Tillard-Charbonnel, A. Manteghetti, L. Monconduit, C. Belin, Synthesis and Crystal Structure of M₁₁X₁₀ Compounds, M=Sr, Ba and X=Bi, Sb. Electronic Requirements and Chemical Bonding, J. Solid State Chem. 164 (2002) 169–175.
doi:10.1006/jssc.2001.9470.
- [11] B. Li, A.V. Mudring, J.D. Corbett, Valence Compounds versus Metals. Synthesis, Characterization, and Electronic Structures of Cubic Ae₄Pn₃ Phases in the Systems Ae = Ca, Sr, Ba, Eu; Pn = As, Sb, Bi, Inorg. Chem. 42 (2003) 6940–6945.
doi:10.1021/ic0301472.
- [12] B. Eisenmann, K. Deller, Zur Kenntnis der Erdalkaliantimonide und -wismutide Sr₂Bi, Ba₂Sb, Sr₅Bi₃, Ba₅Sb₃ und Ba₅Bi₃, Zeitschrift Fur Naturforsch. - Sect. B J. Chem. Sci. 30 (1975) 66–72. doi:10.1515/znb-1975-1-218.
- [13] M. Martinez-Ripoll, A. Haase, G. Brauer, The crystal structure of Ba₂Bi, Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem. 30 (1974) 2003–2004.
doi:10.1107/S0365110X55000716.
- [14] J. Evers, G. Oehlinger, B. Sendlinger, A. Weiss, M. Schmidt, P. Schramel, Lattice parameter of a high purity barium wire extruded in ultrahigh vacuum, J. Alloys Compd. 182 (1992) 175–187. doi:10.1016/0925-8388(92)90586-X.
- [15] H. Kim, D.A. Boysen, D.J. Bradwell, B. Chung, K. Jiang, A.A. Tomaszowska, K. Wang,

- 1
2
3
4 W. Wei, D.R. Sadoway, Thermodynamic properties of calcium-bismuth alloys determined
5
6 by emf measurements, *Electrochim. Acta.* 60 (2012) 154–162.
7
8 doi:10.1016/j.electacta.2012.11.063.
9
- 10
11
12 [16] H. Okamoto, Ba-Bi (Barium-Bismuth), 2nd ed., ASM International, Materials Park, 1990.
13
14
- 15 [17] G. Grube, A. Dietrich, Elektrische Leitfähigkeit und Zustandsdiagramm bei binären
16
17 legierungen, *Z. Elektrochem.* 44 (1938) 755–758.
18
19
- 20
21 [18] S. Ponou, T.F. Fässler, Nonclassical bonding in the novel structure of Ba₂Bi₃ and
22
23 unexpected site preference in the coloring variant Ba₂BiSb₂, *Inorg. Chem.* 43 (2004)
24
25 6124–6126. doi:10.1021/ic0495719.
26
27
- 28
29 [19] E.A. Leon-Escamilla, W.-M. Hurng, E.S. Peterson, J.D. Corbett, Synthesis, Structure, and
30
31 Properties of Ca₁₆Sb₁₁, a Complex Zintl Phase. Twelve Other Isotypic Compounds
32
33 Formed by Divalent Metals and Pnictogens, *Inorg. Chem.* 36 (1997) 703–710.
34
35
36 doi:10.1021/ic961035w.
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

TABLES and FIGURES

Table 1. Change in partial molar entropy and enthalpy of barium calculated from linear fits to the emf data versus temperature for $x_{\text{Ba}} = 0.05\text{--}0.80$, where the slopes and intercepts are $\partial E_{\text{cell}}/\partial T$ and $T^2(\partial(E_{\text{cell}}/T)/\partial T)$, respectively. The $\text{adj-}R^2$ value for each linear fit is reported.

x_{Ba}	T (K)	$\partial E_{\text{cell}}/\partial T$ ($\mu\text{V K}^{-1}$)	$T^2(\partial(E_{\text{cell}}/T)/\partial T)$ (mV)	$\Delta\bar{S}_{\text{Ba}}$ ($\text{J mol}^{-1} \text{K}^{-1}$)	$\Delta\bar{H}_{\text{Ba}}$ (kJ mol^{-1})	$\text{adj-}R^2$
0.05	707-938	197 $\pm$ 6	1011 $\pm$ 5	38.0	-195.1	0.96
0.10	704-1048	137 $\pm$ 1	1031 $\pm$ 1	26.4	-199.0	0.99
0.15	728-1048	125 $\pm$ 2	1005 $\pm$ 2	24.1	-193.9	0.99
0.20	809-1048	94 $\pm$ 7	984 $\pm$ 6	18.1	-189.9	0.90
0.25	881-1048	73.4 $\pm$ 5	961 $\pm$ 5	14.2	-185.4	0.93
	704-881	-480 $\pm$ 14	1448 $\pm$ 13	-92.6	-279.4	0.98
0.30	864-1048	54.7 $\pm$ 7	958 $\pm$ 7	105.6	-184.8	0.80
	704-864	-614 $\pm$ 43	1545 $\pm$ 34	-118.5	-298.1	0.93
0.35	875-1033	51.8 $\pm$ 7	932 $\pm$ 6	10.0	-179.8	0.80
	691-875	19.8 $\pm$ 1	961 $\pm$ 6	3.8	-185.4	0.85
0.40	913-1033	44.6 $\pm$ 11	896 $\pm$ 10	8.6	-172.9	0.81
	812-913	-501 $\pm$ 71	1398 $\pm$ 61	-96.7	-270.0	0.91
	691-812	-29.4 $\pm$ 7	1006 $\pm$ 8	-5.7	-194.1	0.84
0.45	715-961	-215 $\pm$ 9	1085 $\pm$ 7	-41.5	-209.4	0.98
0.50	715-961	-271 $\pm$ 17	1097 $\pm$ 14	-52.3	-211.7	0.97
0.55	740-1041	-201 $\pm$ 17	967 $\pm$ 15	-38.8	-186.6	0.92
0.70	770-957	6.9 $\pm$ 0.6	645 $\pm$ 12	1.3	-124.5	0.84
0.75	866-1030	-542 $\pm$ 40	683 $\pm$ 38	-104.6	-131.8	0.96
	697-866	-2900 $\pm$ 155	2716 $\pm$ 121	-559.6	-524.1	0.98
0.80	862-1034	222 $\pm$ 15	-206 $\pm$ 14	42.8	-39.8	0.97
	717-862	-530 $\pm$ 49	444 $\pm$ 38	-102.3	-85.7	0.96

Table 2. Measured emf values, the natural log of activity of Ba, and the excess partial molar Gibbs free energy of Ba-Bi alloys over $x_{\text{Ba}} = 0.05\text{--}0.80$ at 773 K, 873 K, and 973K.

x_{Ba}	E (V)			$\ln a_{\text{Ba}}$			$\bar{G}_{\text{Ba}}^{\text{E}}$ (kJ mol ⁻¹)		
	773 K	873 K	973 K	773 K	873 K	973 K	773 K	873 K	973 K
0.05	1.164	1.183	1.203	-35.0	-31.5	-28.7	-205	-206	-208
0.10	1.137	1.150	1.164	-34.1	-30.6	-27.8	-205	-205	-206
0.15	1.101	1.114	1.127	-33.0	-29.6	-26.9	-200	-201	-202
0.20	1.075	1.066	1.076	-32.2	-28.3	-25.7	-197	-194	-194
0.25	1.075	1.027	1.032	-32.2	-27.3	-24.6	-198	-188	-188
0.30	1.069	1.006	1.011	-32.0	-26.7	-24.1	-198	-185	-185
0.35	0.986	0.980	0.982	-29.6	-26.1	-23.4	-184	-181	-181
0.40	0.986	0.960	0.939	-29.6	-25.5	-22.4	-184	-178	-173
0.45	0.924	0.899	0.861	-27.7	-23.9	-20.5	-173	-167	-159
0.50	0.877	0.855	0.847	-26.3	-22.7	-20.2	-164	-160	-157
0.55	0.816	0.795	0.773	-24.5	-21.1	-18.4	-154	-149	-144
0.70	0.647	0.651	0.648	-19.4	-17.3	-15.5	-122	-123	-122
0.75	0.474	0.209	0.155	-14.2	-5.6	-3.7	-90	-38	-27
0.80	0.034	0.000	0.010	-1.02	0.0	-0.24	-5	1	0

Table 3. The estimated emf, partial molar Gibbs free energy, and activity values of Ba in Bi at 1123 K based on the extrapolation of the linear fit, compared to the results by Delcet *et al.* [3].

x_{Ba}	This study			Delcet <i>et al.</i>		
	E_{cell} (V)	$\Delta\bar{G}_{\text{Ba}}$ (kJ mol ⁻¹)	a_{Ba}	E_{cell} (V)	$\Delta\bar{G}_{\text{Ba}}$ (kJ mol ⁻¹)	a_{Ba}
0.05	1.23	-237.8	8.7×10^{-12}	1.30	-250.0	2.4×10^{-12}
0.10	1.18	-228.6	2.3×10^{-11}	1.24	-238.9	7.7×10^{-12}
0.15	1.15	-221.0	5.3×10^{-11}	1.18	-227.9	2.5×10^{-11}
0.20	1.09	-210.3	1.7×10^{-10}	1.12	-215.6	9.4×10^{-11}

Table 4. Summary of the crystal structures in Ba-Bi system reported in this work [8-14].

Phase	x_{Ba}	Density (g cm ⁻³)	Space group (Pearson symbol)	Lattice Parameters (nm) (°)		Ref.
Bi	0.00	9.81	$R\bar{3}m$ (<i>hR6</i>)	a=0.455 b=0.455 c=1.19	$\alpha=90$ $\beta=90$ $\gamma=120$	[8]
BaBi ₃	0.25	9.14	$P4\bar{m}mm$ (<i>tP4</i>)	a=0.519 b=0.519 c=0.516	$\alpha=90$ $\beta=90$ $\gamma=90$	[9]
Ba ₁₁ Bi ₁₀	0.52	7.06	$I4\bar{m}mm$ (<i>tl84</i>)	a=1.323 b=1.323 c=1.936	$\alpha=90$ $\beta=90$ $\gamma=90$	[10]
Ba ₄ Bi ₃	0.57	6.65	$I\bar{4}3d$ (<i>cl28</i>)	a=1.055 b=1.055 c=1.055	$\alpha=90$ $\beta=90$ $\gamma=90$	[11]
Ba ₅ Bi ₃	0.63	6.30	$P6_3\bar{m}cm$ (<i>hP16</i>)	a=1.013 b=1.013 c=0.779	$\alpha=90$ $\beta=90$ $\gamma=120$	[12]
Ba ₂ Bi	0.66	6.20	$I4\bar{m}mm$ (<i>tl12</i>)	a=0.526 b=0.526 c=1.870	$\alpha=90$ $\beta=90$ $\gamma=90$	[13]
Ba	1.00	3.59	$Im\bar{3}m$ (<i>cl2</i>)	a=0.503 b=0.503 c=0.503	$\alpha=90$ $\beta=90$ $\gamma=90$	[14]

Table 5. Summary of transition temperatures T_{trs} (K) determined by differential scanning calorimetry over multiple scan rates and the standard error in the parenthesis.

x_{Ba}	T_{trs} (K)					
	I	II	III	IV	V	Liquidus
0.05	538(1)	—	—	—	—	—
0.10	547(4)	—	—	—	—	—
0.15	538(1)	—	—	—	—	—
0.20	538(1)	—	—	—	—	813(9)
0.25	537(1)	—	—	—	—	863(14)
0.30	545(3)	—	—	—	—	—
0.35	538(2)	853(3)	—	—	—	—
0.40	—	846(4)	—	—	—	926(8)
0.45	—	847(1)	—	—	—	—
0.50	—	844(2)	—	—	—	1043(3)
0.55	—	—	1010(8)	—	—	1067(1)
0.60	—	—	1004(9)	—	—	1056(3)
0.70	—	—	—	—	—	972(3)
0.75	—	—	—	—	—	969(4)
0.80	—	—	—	—	797(1)	958(15)
0.85	—	—	—	—	—	935(11)
0.90	—	—	—	—	796(4)	904(24)
0.95	—	—	—	873(9)	796(1)	—

Table 6. Reactions assigned to the transition temperatures determined by DSC in Table 6 and emf measurements, in comparison to the previous report by Okamoto [16].

Transition	Reaction	T_{trs} (K)			Type
		DSC	Emf	Okamoto	
I	liquid = Bi + BaBi ₃	537(5)	—	535	Eutectic
*	liquid + ? = BaBi ₃	—	—	720	Peritectic
II	liquid = BaBi ₃ + Ba ₁₁ Bi ₁₀	846(4)	843(6)	—	Eutectic
III	Ba ₄ Bi ₃ (rt) = Ba ₄ Bi ₃ (ht)	1007(9)	—	—	Allotropic
IV	liquid = Ba ₂ Bi + Ba (ht)	873(9)	864(2)	—	Eutectic
V	Ba (rt) = Ba (ht)	796(4)	—	—	Allotropic

*: undefined phase transition reaction reported by Okamoto at 720 K.

Figure 1. Illustration of the $\text{Ba-Bi}(x_{\text{Ba}} = 0.05)|\text{CaF}_2\text{-BaF}_2|\text{Ba}(\text{in Bi})$ or $\text{Ba}(\text{s})|\text{CaF}_2\text{-BaF}_2|\text{Ba-Bi}(x_{\text{Ba}} = 0.05)$ cells used for emf measurements, with the positions of thermocouple, working electrodes (WEs), and reference electrodes (REs) indicated.

Figure 2a.

Figure 2b.

Figure 2. (a) The measured emf values (E_I) and temperature as a function of time upon cooling and reheating a Ba-Bi($x_{Ba} = 0.05$)|CaF₂-BaF₂|Ba(in Bi) cell with Ba-Bi alloys $x_{Ba} = 0.05$, 0.10, and 0.20 and (b) the measured emf values (E_{II}) using a Ba(s)|CaF₂-BaF₂(s)|Ba-Bi($x_{Ba} = 0.05$) cell.

Figure 3a.

Figure 3b.

Figure 3c.

Figure 3. The emf as a function of temperature for (a) $x_{\text{Ba}} = 0.05$ to 0.30 , (b) $x_{\text{Ba}} = 0.35$ to 0.55 and (c) $x_{\text{Ba}} = 0.70$ to 0.80 , where solid lines represent linear fits and dashed lines are a visual guide.

Figure 4a.

Figure 4b.

Figure 4c.

Figure 4. Plots of the (a) measured emf values (E_{cell}), (b) the natural log of the activity of Ba ($\ln a_{\text{Ba}}$), and (c) the calculated excess partial molar Gibbs free energy of Ba as a function of mole fraction at 773 K.

Figure 5a.

Figure 5b.

Figure 5. Representative powder XRD patterns of Ba-Bi alloys (a) $x_{\text{Ba}} = 0.05\text{--}0.50$ and (b) $x_{\text{Ba}} = 0.60\text{--}0.90$, compared to the reported diffraction patterns of Ba-Bi intermetallic compounds (*) [8-14].

Figure 6. Representative differential scanning calorimetry data during heating (H) or cooling (C) cycle at 20 K min^{-1} for Ba-Bi alloys $x_{\text{Ba}} = 0.05\text{--}0.95$, major transition temperatures are designated by Roman numerals (I-V) and by * for liquidus transitions.

Figure 7. Revised Ba-Bi phase diagram based upon differential scanning calorimetry (DSC) and electromotive force (emf) measurements, dashed line represents metastable Bi phase up to $x_{Ba} = 0.52$.