Thermodynamic Properties of Strontium-Bismuth Alloys Determined by Electromotive Force Measurements

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ABSTRACT

The thermodynamic properties of Sr-Bi alloys were determined by electromotive force (emf) measurements to evaluate the viability of liquid bismuth metal as a medium for separating alkali/alkaline-earth fission products from molten salt electrolyte. A $\text{Sr(s)}|\text{CaF}_2\text{-SrF}_2|\text{Sr(in Bi)}$ cell was used to measure emf values at 748–1023 K for thirteen Sr-Bi alloys at mole fractions $0.05 \leq x_{\text{Sr}} \leq 0.75$. Activity values of strontium in bismuth were determined at 788 K, 888 K, and 988 K as well as the partial molar entropy and enthalpy at each composition. Reproducible emf values within $\pm 5\text{mV}$ were obtained up to $x_{\text{Sr}} = 0.35$ during cooling-heating cycle. At higher mole fractions ($x_{\text{Sr}} \geq 0.40$), the emf values exhibited increased hysteresis during the thermal cycles due to the strong tendency of the alloys to form meta-stable phases. The non-equilibrium phase behavior of Sr-Bi alloys was verified by X-ray diffraction (XRD), differential scanning calorimetry (DSC) and microstructural analyses. Compared to the existing equilibrium phase diagram, two additional phases of Sr_2Bi_3 and Sr_4Bi_3 were identified and discussed. Liquid-state solubility of Sr was 15–40 mol% at 788–988 K and the activity values were as low as 10^{-13} at 788 K, implying strong chemical interactions between Sr and Bi.

1. INTRODUCTION

Electrochemical separation using molten salt electrolytes (e.g., LiCl-KCl) is currently one of the most promising techniques for separating uranium and transuranics from metallic used nuclear fuels [1]. However, the process has the inevitable consequence of accumulating alkali/alkaline-earth fission products in the molten salt electrolyte because alkali/alkaline-earth metals (Ba, Sr, and Cs) have the strongest tendency to oxidize during electrolysis. Periodic replacement of the electrolyte containing these fission products results in chloride wastes that can limit the development of a ceramic wasteform for long-term disposal and increase the volume of nuclear waste [2]. In addition, the alkali/alkaline fission products Sr and Cs pose serious environmental challenges as they have short half-lives (around 30 years) and highest heat densities [3]. In our previous work, the separation of barium from quaternary BaCl₂-LiCl-CaCl₂-NaCl (16-29-35-20 mol%) electrolyte was achieved due to the extremely low thermodynamic activity of Ba in the liquid Bi electrode compared to Li, Ca, and Na, implying strong atomic interactions between Ba and Bi [4]. In efforts to separate radiotoxic Sr species from molten salt electrolyte, the thermodynamic properties of Sr-Bi alloys at 748–1023 K were examined using electromotive force (emf) techniques to evaluate the viability of using liquid bismuth electrodes for the separation of Sr.

Constructing an electrochemical cell to effectively measure emf values for Sr-Bi alloys can be technically challenging due to (i) the high reactivity of pure Sr as well as Sr-Bi alloys which can degrade the electrolytes or cell components during emf measurements, and (ii) the high melting temperatures of pure Sr ($T_{m, Sr} = 1042$ K) and Sr-Bi alloys ($T_{liquidus}$ up to 1218 K) [5]. In recent studies, solid-state CaF₂ electrolyte has been utilized in determining the thermodynamic properties of Ca-Bi, Ca-Sb, and Ca-Mg alloys at 723–1100 K [6–8], employing

the high stability of CaF_2 electrolyte in emf measurements of calcium alloys. Delcet and Egan also determined the emf values of Ca-Ag and Ca-In alloys using single-crystal CaF_2 at 1073 K via coulometric titration techniques and derived thermodynamic activity values of calcium [9]. The solid-state CaF_2 is well known to have substantial ionic conductivity ($1.5 \times 10^{-3} \text{ S cm}^{-1}$ at 1073 K), suitable for emf measurements [10,11].

In the present study, the investigation of Sr-Bi alloys required using CaF_2 - SrF_2 (97-3 mol%) instead of the pure CaF_2 electrolyte to account for the change in electroactive species. According to the analysis of standard electrode potentials in the fluoride system at 873 K (Figure 1a), CaF_2 is more stable than SrF_2 and thus, strontium ions are expected to be the most electroactive species in the CaF_2 - SrF_2 binary electrolyte. In contrast, SrCl_2 is more stable than CaCl_2 in the chloride system (Figure 1b) and thus, calcium becomes the most electroactive species, invalidating the stable emf measurements of Sr-based alloys in CaCl_2 - SrCl_2 electrolyte due to the side reactions (e.g., $\text{Sr} + \text{CaCl}_2 = \text{SrCl}_2 + \text{Ca}$, $\Delta_r G = -28.9 \text{ kJ}$ at 873 K) [12].

[Figure 1]

The temperature-dependent thermodynamic properties of Sr-Bi alloys were investigated using the following electrochemical cell:

, where pure strontium acts as the reference electrode (RE), solid CaF_2 - SrF_2 (97-3 mol%) as the electrolyte, and Sr-Bi alloys as working electrodes (WE). In this electrochemical cell, the half-cell reactions are

, and the overall cell reaction is

The change in partial molar Gibbs energy of strontium, $\Delta\bar{G}_{\text{Sr}}$, for this reaction is given by

$$\Delta\bar{G}_{\text{Sr}} = \bar{G}_{\text{Sr(in Bi)}} - G_{\text{Sr(s)}}^0 = RT \ln a_{\text{Sr}} \quad (4)$$

, where $\bar{G}_{\text{Sr(in Bi)}}$ is the partial molar Gibbs energy of strontium in bismuth, $G_{\text{Sr(s)}}^0$ is the free energy of pure strontium, R is the ideal gas constant, T is the temperature, and a_{Sr} is the activity of strontium in bismuth. By applying the Nernst equation to Eq. (4), the change in partial molar Gibbs energy of strontium in a given bismuth alloy (and thus activity) is directly related to the cell emf E_{cell} :

$$E_{\text{cell}} = -\frac{\Delta\bar{G}_{\text{Sr}}}{zF} = -\left(\frac{RT}{zF}\right) \ln a_{\text{Sr}} \quad (5)$$

, where F is the Faraday constant and z is the number of electrons transferred in the reaction ($z = 2$).

2. EXPERIMENTAL

2.1. Electrochemical cell components and assembly

Solid CaF_2 - SrF_2 (97-3 mol%) electrolyte was prepared by ball-milling 350 g of high-purity CaF_2 (Alfa Aesar, Stock No. 11055), 16.9 g of high-purity SrF_2 (Sigma Aldrich, Stock No. 450030), and 25 g of polyvinyl alcohol binder (Sigma Aldrich, Stock No. 341584) in isopropanol for 24 h. The mixture was dried in air for 24 h and approximately 130 g of powder was taken and

uniaxially pressed at 30 MPa into a pellet 75 mm $\times$ 17 mm in diameter and thickness. Seven wells (each with 11.2 mm $\times$ 12 mm in diameter and depth) were drilled into the pellet with one well in the center and six wells evenly spaced 25.4 mm away from the center (Figure 2a). Similarly, seven caps were fabricated from 4 g of the mixture (19 mm $\times$ 10 mm in diameter and height) with a 1.1 mm hole drilled through the center. These green pellets were then fired in air at 393 K for 12 h to remove moisture, 823 K for 12 h to burn away the polyvinyl alcohol binder, and 1273 K for 3 h to sinter. The sintered CaF₂-SrF₂ electrolyte was confirmed to have formed a single-phase solid solution (fluorite phase) by an x-ray diffractometer (XRD) as shown in Figure 2b.

[Figure 2]

Strontium-bismuth alloys at specific compositions were fabricated from bismuth pieces (Sigma Aldrich, Stock No. 556130) and strontium ingot (Sigma Aldrich, Stock No. 343730) using an arc melter (MAM1, Edmund Buhler GmbH) under argon atmosphere. The alloys were machined into a cylindrical shape (10 mm $\times$ 7 mm in diameter and thickness) with a 1.1 mm center hole for insertion of the electrical lead wire (tungsten).

Final assembly of the electrochemical cell was performed in a glovebox under an inert argon environment (O₂ concentration < 0.5 ppm) to mitigate the rapid oxidation of Sr and Sr-Bi alloys. The CaF₂-SrF₂ electrolyte was placed in an alumina crucible (8.2 cm diameter $\times$ 3.0 cm height) and tungsten wires (1 mm $\times$ 46 cm in diameter and length) were inserted into alumina tube sheaths, sealed at the top with epoxy, passed through the stainless steel test chamber, through the CaF₂-SrF₂ caps, and into the electrodes. The caps were installed to minimize the contamination of alloys during the measurements by physically blocking the vapor-phase transport of strontium.

2.2. Emf measurements

The test chamber was then sealed, removed from the glovebox, loaded into a crucible furnace, and evacuated to ~ 1 Pa. The test chamber was heated at 373 K for 12 h, at 543 K for 12 h under vacuum to remove residual moisture and oxygen, purged three times with high purity argon, and finally heated to 1023 K under flowing argon (~ 10 mL min $^{-1}$) atmosphere to melt the electrodes and establish electrical contact with the tungsten wires.

Emf measurements were performed by measuring the potential difference between the reference electrode and each working electrode (Sr-Bi alloys) sequentially in 180 s intervals during thermal cycles using a potentiostat-galvanostat (Autolab PGSTAT302N, Metrohm AG). Emf data were collected throughout a cooling and reheating cycle between 1023 K and 748 K in 25 K increments. The cell temperature was held constant at each increment for 1.5 h to reach thermal and electrochemical equilibria and ramped at ± 5 K min $^{-1}$ between increments. The cell temperature was measured using a thermocouple (ASTM type-K) located at the center of the electrolyte, and thermocouple data acquisition system (NI 9211, National Instruments).

2.3 Characterization of Sr-Bi alloys

Crystal structures of the Sr-Bi alloys were characterized using an X-ray diffractometer (XRD, PANalytical Empyrean). For equilibrium phase determination, Sr-Bi alloys were annealed at ~ 15 K below their solidus temperatures for 24 h. Samples were prepared by grinding Sr-Bi alloys into a fine powder using a mortar and pestle in a glovebox under inert argon atmosphere. The powder samples were coated with mineral oil in order to minimize the oxidation of the alloys during the measurements. A broad amorphous background from mineral

oil was present in the XRD spectra at low angles ($10^\circ \leq 2\theta \leq 20^\circ$), but was subtracted to facilitate the identification of crystalline phase peaks of Sr-Bi alloys.

The morphology and microstructure analysis of the annealed alloys was performed using scanning electron microscope (SEM, FEI Quanta 200) fitted with energy dispersive spectroscopy (EDS) capabilities to identify the phases and their compositions. Samples were mounted in epoxy, ground, and polished with emery papers of 100–2000 grit sizes using isopropanol.

Differential scanning calorimetry (DSC) and thermal gravimetric (TG) analyses were performed using a thermal analyzer (Netzsch Instruments, STA 449 F3 Jupiter) to detect phase transition temperatures of Sr-Bi alloys to complement the phase behavior determined by the emf techniques. About 20–50 mg of each annealed alloy sample was placed in an alumina crucible with a thin tungsten foil interlayer (4.8 mm diameter $\times$ 0.1 mm thickness) that acted as a reaction barrier between the Sr-Bi alloy and alumina crucible. Thermal analyses were conducted at multiple scan rates (7–20 K min⁻¹) and the phase transition temperature was determined based on onset temperatures at various scan rates by extrapolating the onset temperatures to the scan rate of 0 K min⁻¹ [13]. The Sr-Bi alloys with $x_{\text{Sr}} \geq 0.35$ were found to damage platinum parts of TG-DSC sensor, possibly due to the vapor phase transport of Sr vapors, and were excluded for further measurements.

3. RESULTS AND DATA ANALYSIS

3.1. Emf Measurements

The use of pure strontium metal as reference electrode caused rapid degradation of the solid-state CaF₂-SrF₂ electrolyte, resulting in a poor reproducibility of the emf measurements as well as a decline in reference electrode stability. Instead, a less reactive Sr-Bi alloy (mole

fraction, $x_{\text{Sr}} = 0.10$) was employed as the reference electrode in emf measurements of various alloy compositions using a $\text{Sr-Bi}(x_{\text{Sr}} = 0.10)|\text{CaF}_2\text{-SrF}_2|\text{Sr}(\text{in Bi})$ cell, in a manner similar to Newhouse *et al.* [8]. The choice the Sr-Bi alloy $x_{\text{Sr}} = 0.10$ was advantageous because this alloy composition (1) experiences no phase changes at 700–1023 K, resulting in a linear thermal emf (dE_{cell}/dT); (2) produced highly reproducible emf values for various Sr-Bi alloys during the thermal cycle; and (3) their potential difference remained less than ± 5 mV throughout the emf measurements, implying an excellent stability as a reference electrode (Figure 3a). In separate experiments, the electrode potential of the Sr-Bi alloy $x_{\text{Sr}} = 0.10$ was determined against pure Sr using a $\text{Sr}(\text{s})|\text{CaF}_2\text{-SrF}_2|\text{Sr-Bi}(x_{\text{Sr}} = 0.10)$ cell (Figure 3b). Using the linear fit of this measurement at $x_{\text{Sr}} = 0.10$ (Figure 3b), the emf values of Sr-Bi alloys E_{cell} are reported relative to pure Sr metal.

[Figure 3]

The variation of emf with temperature and composition for Sr-Bi alloys ($x_{\text{Sr}} = 0.05\text{--}0.75$) is displayed in Figure 4a-c, obtained upon cooling and reheating the electrochemical cells. In general, the emf values were in close agreement between the cooling and heating with less than a 5 mV difference up to $x_{\text{Sr}} = 0.30$. In Figure 4a, the emf varies linearly with respect to temperature and increases as x_{Sr} decreases above the liquidus (liquid = liquid + $\text{SrBi}_3(\text{s})$); below the liquidus, the activity of strontium does not change with composition and the emf values collapse onto the same line. In Figure 4b, mole fraction $x_{\text{Sr}} = 0.30$ exhibits two phase transitions, a liquidus (liquid = liquid + Sr_2Bi_3) at 908 K and a solidus (liquid + $\text{Sr}_2\text{Bi}_3 = \text{SrBi}_3 + \text{Sr}_2\text{Bi}_3$) at 843 K.

Emf values of alloys with high strontium content ($0.35 \leq x_{\text{Sr}} \leq 0.75$) exhibited increased hysteresis between the heating-cooling cycles up to a 25 mV difference possibly due to the

increased reactivity. For this reason, emf data for high Sr alloys ($x_{\text{Sr}} \geq 0.35$) were collected from the first cooling cycle only (Figure 4b-c). Mole fraction $x_{\text{Sr}} = 0.45$ exhibited a solidus transition (liquid + $\text{Sr}_{11}\text{Bi}_{10} = \text{Sr}_2\text{Bi}_3 + \text{Sr}_{11}\text{Bi}_{10}$) at 908 K (Figure 4b); mole fraction $x_{\text{Sr}} = 0.55$ exhibited a solidus phase transition (liquid + $\text{Sr}_4\text{Bi}_3 = \text{Sr}_{11}\text{Bi}_{10} + \text{Sr}_4\text{Bi}_3$) at ~985 K (Figure 4c). The transition reactions were inferred based on the observed crystal structures at each composition, which will be discussed later in section 3.2. It should be noted that the observed crystal structures of the Sr_2Bi_3 and Sr_4Bi_3 phases are well reported in the database [14,15], but not included in the most recent Sr-Bi equilibrium phase diagrams. It is probable that these structures exist as meta-stable phases in the present study.

[Figure 4]

The change in the partial molar entropy of strontium, $\Delta\bar{S}_{\text{Sr}}$, was calculated from linear fits of the measured emf data in Figure 4a-c using the thermodynamic relation:

$$\Delta\bar{S}_{\text{Sr}} = -\left(\frac{\partial\Delta\bar{G}_{\text{Sr}}}{\partial T}\right)_P = zF\left(\frac{\partial E_{\text{cell}}}{\partial T}\right)_P. \quad (6)$$

Similarly, the change in the partial molar enthalpy, $\Delta\bar{H}_{\text{Sr}}$, was calculated using the Gibbs-Helmholtz relation:

$$\Delta\bar{H}_{\text{Sr}} = -T^2\left(\frac{\partial(\Delta\bar{G}_{\text{Sr}}/T)}{\partial T}\right)_P = zFT^2\left(\frac{\partial(E_{\text{cell}}/T)}{\partial T}\right)_P = -zF\left(\frac{\partial(E_{\text{cell}}/T)}{\partial(1/T)}\right). \quad (7)$$

As shown in Figure 5 for alloys $x_{\text{Sr}} = 0.05\text{--}0.15$, the change in partial molar enthalpy was estimated based on the slopes by plotting E_{cell}/T versus $1/T$. The estimated partial molar quantities as well as the linear fits of temperature-dependent emf values are summarized in Table

1.

[Figure 5]

[Table 1]

Using the Nernst equation, the activity of Sr in Bi, a_{Sr} , was calculated for specific temperatures of 788 K, 888 K, and 988 K using the measured emf values:

$$\ln a_{\text{Sr}} = -\frac{zFE_{\text{cell}}}{RT}. \quad (8)$$

The excess partial molar Gibbs energy of Sr, $\overline{G}_{\text{Sr}}^E$, was then calculated from the activity data:

$$\overline{G}_{\text{Sr}}^E = RT \ln \gamma_{\text{Sr}} = RT(\ln a_{\text{Sr}} - \ln x_{\text{Sr}}) \quad (9)$$

, where γ_{Sr} is the activity coefficient. The results of emf values, natural log of the activity, and the excess partial molar Gibbs energy are summarized in Table 2 and are presented graphically in Figure 6 at 888 K.

[Table 2]

[Figure 6]

Figures 6a displays the emf values as a function of strontium mole fraction with the phase compositions of each intermetallic compound as well as liquidus composition at 888K. In the two-phase region (liquid + Sr_2Bi_3) at $0.26 < x_{\text{Sr}} < 0.40$, the emf is nearly constant because chemical potential (or activity) of Sr becomes invariant with respect to x_{Sr} in two-phase regions (Figure 6a-b). However, in the two-phase region ($\text{Sr}_2\text{Bi}_3 + \text{Sr}_{11}\text{Bi}_{10}$) at $0.40 < x_{\text{Sr}} < 0.52$, the different emf values were obtained, indicating non-equilibrium phase behavior. In the Sr-Bi system, a large excess partial molar Gibbs energy (as low as -176 kJ mol^{-1} at $x_{\text{Sr}} = 0.05$) was obtained, indicating a highly non-ideal solution behavior due to the strong chemical interactions between Sr and Bi (Figure 6c).

According to the equilibrium phase diagram [5], we anticipate that the emf values will approach zero in the two-phase composition domain ($\text{Sr}_2\text{Bi} + \text{Sr}$) at $x_{\text{Sr}} > 0.67$ due to the presence of pure strontium phase, as observed in the proxy Ca-Bi system [6]. However, the emf value at $x_{\text{Sr}} = 0.75$ remained at ~ 0.75 V versus pure Sr (Figure 6a). This discrepancy was found to be due to the formation of meta-stable phases at this composition, and the alloy $x_{\text{Sr}} = 0.75$ was comprised of Sr_2Bi , Sr_5Bi_3 , and Sr_4Bi_3 without pure Sr phase.

3.2 Structural characterization and meta-stable phases

Crystal structures of known phases in the Sr-Bi system are summarized in Table 3 [14–16]. X-ray diffraction patterns for Sr-Bi alloys are presented in Figure 7. In general, multiple meta-stable phases were present in Sr-Bi alloy systems at mole fractions $x_{\text{Sr}} \geq 0.25$, which may explain the increased hysteresis in the emf measurements during the cooling-heating cycle as well as unusually high emf values at high strontium concentrations ($x_{\text{Sr}} > 0.67$).

[Table 3]

[Figure 7]

Figure 7a indicates the presence of bismuth phase ($R\bar{3}m$) up to $x_{\text{Sr}} = 0.40$ although the equilibrium phase diagram predicts its stability only up to $x_{\text{Sr}} = 0.25$ [5,17]. Further annealing at ~ 15 K below the solidus temperature for $x_{\text{Sr}} = 0.40$ ($T_{\text{solidus}} = 840$ K) was performed to remove the meta-stable Bi phase, but only a slight reduction in the intensity of Bi phase was observed even after 168 h of annealing, implying that much longer annealing time may be necessary to achieve equilibrium phases. The presence of the Sr_2Bi_3 ($Pnna$) and Sr_4Bi_3 ($I\bar{4}3d$) phases was evident as shown in Figure 7b. For instance, mole fraction $x_{\text{Sr}} = 0.65$ is expected to be in two-

phase equilibrium (Sr_5Bi_3 and Sr_2Bi) [5,17], however, this alloy composition was found to be comprised of three phases (Sr_5Bi_3 , Sr_2Bi , and Sr_4Bi_3) via XRD and SEM/EDS analyses.

Notably absent from the XRD analysis was the presence of pure Sr phase peaks at $x_{\text{Sr}} > 0.67$. Mole fractions $x_{\text{Sr}} = 0.75$ and 0.80 were comprised of Sr_2Bi , Sr_4Bi_3 and Sr_5Bi_3 (Figure 7b), deviating from the equilibrium phase behavior (Sr_2Bi and Sr) [5,17]. These phase analyses explain the abnormally high emf values $0.57\text{--}0.80$ V at $x_{\text{Sr}} = 0.75$ (see Figure 4c and Figure 6a) due to the formation of meta-stable phases in emf measurements.

The presence of meta-stable phases at selected compositions was also investigated through microstructural analysis of the Sr-Bi alloys using SEM/EDS. For example, a back-scattered SEM image obtained from $x_{\text{Sr}} = 0.25$ confirmed the formation of three distinct phases of Bi, SrBi_3 , and Sr_2Bi_3 based on the chemical analysis by EDS at each phase (Figure 8). The SEM/EDS results agree the with XRD analysis, although this alloy composition is expected to form a single-phase line compound of SrBi_3 . Our structural phase analyses by XRD and SEM/EDS suggest that Sr-Bi alloys exhibit a strong tendency to form various meta-stable phases.

[Figure 8]

3.3 Thermal analysis

Thermal analyses at selected alloy compositions ($0.05 \leq x_{\text{Sr}} \leq 0.30$) were conducted at various heating rates of $7\text{--}20$ K min^{-1} . In Figure 9, a representative thermmogram is presented at 7 K min^{-1} . At mole fractions up to $x_{\text{Sr}} = 0.25$, two major transition temperatures were apparent: one related to the melting of Bi phase at $\sim 543 (\pm 2)$ K and the other to the liquidus (liquid = liquid + SrBi_3). The measured melting temperature of Bi was in excellent agreement with the

melting temperature of pure bismuth at 544 K. The phase transition temperatures determined by DSC and emf measurements are summarized in Table 4. The liquidus temperatures determined by emf measurements and thermal analysis agree within 7 K.

At $x_{\text{Sr}} = 0.30$, three transition temperatures were observed: the first at 543 K is related to the melting of meta-stable Bi in accordance with the XRD measurements, the liquidus transition at ~917 K, and the solidus transition at ~843 K (Figure 9). During the solidus transition, the following two reactions are probable: $[\text{liquid} + \text{Sr}_2\text{Bi}_3 = \text{SrBi}_3 + \text{Sr}_2\text{Bi}_3]$ or $[\text{liquid} + \text{Sr}_{11}\text{Bi}_{10} = \text{SrBi}_3 + \text{Sr}_2\text{Bi}_3]$.

[Figure 9]

[Table 4]

3.4 Comparison with equilibrium phase diagram

Based on the phase transition temperatures determined by DSC, XRD, and emf measurements, these results were compared with the existing equilibrium phase diagram calculated by Okamoto and Wang [5,17], as shown in Figure 10 [18]. The liquidus temperatures of Sr-Bi alloys at mole fractions $x_{\text{Sr}} < 0.40$ agreed with our measurements within 10 K. In this work, we identified two additional phases of Sr_2Bi_3 , and Sr_4Bi_3 (dashed lines in Figure 10) using XRD.

At high mole fractions ($x_{\text{Sr}} \geq 0.40$), the observed transition temperatures by emf technique deviated substantially from the reported transition temperatures up to 23 K difference. In general, the discrepancy is primarily due to the non-equilibrium phases present in these Sr-Bi alloys, evidenced by the presence of meta-stable phases at these compositions (e.g., Sr_5Bi_3 , Sr_2Bi , and Sr_4Bi_3 at $x_{\text{Sr}} = 0.65$) and by the absence of pure Sr phase at $x_{\text{Sr}} > 0.67$.

At $x_{\text{Sr}} = 0.40$ and 0.45 , this work observed the transition temperature at ~ 906 K while the equilibrium temperature was calculated to be 883 K (~ 23 K difference). This difference can be explained, in part, by the presence of the Sr_2Bi_3 phase that is not considered in the equilibrium phase diagram calculation and/or the strong tendency to form non-equilibrium phases. However, Wang *et al.* attributed this invariant temperature to be the peritectic reaction $[\text{liquid} + \text{Sr}_5\text{Bi}_3 = \text{Sr}_{11}\text{Bi}_{10}]$; Okamoto described this as the allotropic reaction $[\alpha\text{Sr}_{11}\text{Bi}_{10} = \beta\text{Sr}_{11}\text{Bi}_{10}]$. These discrepancies invite a scrutiny into the phase behavior of the Sr-Bi system, possibly through advanced computational and careful experimental approaches.

[Figure 10]

4. CONCLUSIONS

This study has determined thermodynamic properties of the binary Sr-Bi system, including activities, partial molar entropies, enthalpies, and excess Gibbs energies. The liquid-state solubility of Sr in Bi was estimated to be ~ 15 mol% at 788 K and ~ 40 mol% at 988 K. At high Sr compositions ($x_{\text{Sr}} \geq 0.25$), strong non-equilibrium phase behavior was observed; for example, three phases in the binary system and the absent pure Sr phase at $x_{\text{Sr}} > 0.67$. In addition, two additional phases of Sr_2Bi_3 and Sr_4Bi_3 were considered in describing the phase behavior of Sr-Bi system, which are not considered in the most recent Sr-Bi equilibrium phase diagram.

Combining the high liquid-state solubility and the strong chemical interactions between Sr and Bi (a_{Sr} as low as 1.2×10^{-13}), Bi shows promise as an electrode material for separating dissolved strontium ions (Sr^{2+}) from molten salt electrolytes (e.g., LiCl-KCl-SrCl_2).

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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REFERENCES

- [1] Electrometallurgical Techniques for DOE Spent Fuel Treatment: Final Report, National Academy Press, Washington, D.C, 2000.
- [2] M.F. Simpson, Projected Salt Waste Production from a Commercial Pyroprocessing Facility, Science and Technology of Nuclear Installations (2013) Article number: 945858.
- [3] J. Bruno, R.C. Ewing, Spent nuclear fuel, Elements. 2 (2006) 343–349.
- [4] 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.
- [5] H. Okamoto, Supplemental Literature Review of Binary Phase Diagrams: Al-Mg, Bi-Sr, Ce-Cu, Co-Nd, Cu-Nd, Dy-Pb, Fe-Nb, Nd-Pb, Pb-Pr, Pb-Tb, Pd-Sb, and Si-W, JPEDAV. 36 (2015) 183–195.
- [6] H. Kim, D.A. Boysen, D.J. Bradwell, B. Chung, K. Jiang, A.A. Tomaszowska, K. Wang, W. Wei, D.R. Sadoway, Thermodynamic properties of calcium–bismuth alloys determined by emf measurements, Electrochim. Acta. 60 (2011) 154–162.
- [7] S. Poizeau, H. Kim, J.M. Newhouse, B.L. Spatocco, D.R. Sadoway, Determination and modeling of the thermodynamic properties of liquid calcium-antimony alloys, Electrochim. Acta. 76 (2012) 8–15.
- [8] J.M. Newhouse, S. Poizeau, H. Kim, B.L. Spatocco, D.R. Sadoway, Thermodynamic properties of calcium-magnesium alloys determined by emf measurements, Electrochim. Acta. 91 (2013) 293–301.
- [9] J. Delcet, J.J. Egan, Thermodynamics of Liquid Ca-Ag and Ca-In Alloys, J. Less-Common

- Met. Elsevier Sequoia S.A. 59 (1978) 229–236.
- [10] J. Fouletier, H. Seiner, M. Kleitz, J. Delcet, R.J. Heus, J.J. Egan, Electronic Conductivity in Solid CaF at High Temperature, *J. Solid State Chem. J. Appl. Electrochem. This J. J. Chim. Phys. J. Appl. Electrochem. J. Solid State Chem. J. Fouletier J. Solid State Chem.* 125 (1976) 369–217.
- [11] N.I. Sorokin, B.P. Sobolev, Solid-State Fluoride Electrolyte Review, *Crystallogr. Reports.* 52 (2007) 842–863.
- [12] HSC Chemistry 5.1, F. Outokumpu Research Oy, Finland, 2002.
- [13] G.W.H. Hohne, W.F. Hemminger, H.-J. Flammersheim, *Differential Scanning Calorimetry*, 2nd Ed., Springer-Verlag Berlin Heidelberg, 2003.
- [14] R.T. Downs, M. Hall-Wallace, The American Mineralogist Crystal Structure Database, (2003) *American Mineralogist* 88, 247–250.
- [15] G. Bergerhoff, I.D. Brown, *Inorganic Crystal Structure Database (FIZ Karlsruhe)*, (1978).
- [16] H. Okamoto, Bi-Sr (Bismuth-Strontium), *Binary Alloy Phase Diagrams*, 2nd Ed. ASM International. 1990.
- [17] Y. Wang, J. Xin, C. Chen, S. Liu, B. Hu, Y. Du, Thermodynamic assessment of the Sr-In and Sr-Bi systems supported by first-principles calculations, *Calphad.* 45 (2014) 49–54.
- [18] J.O. Andersson, T. Helander, L. Hoglund, P.F. Shi, B. Sundman, Thermo-Calc and DICTRA, Computational tools for materials science, *Calphad.* 26 (2002) 273–312.

TABLES AND FIGURES

Table 1. Measured partial molar entropies and partial molar enthalpies for Sr-Bi alloy compositions $x_{\text{Sr}} = 0.05$ to $x_{\text{Sr}} = 0.75$ as well as linear fits of emf values.

x_{Sr}	T (K)	$\partial E_{\text{cell}}/\partial T$ ($\mu\text{V K}^{-1}$)	$\partial(E_{\text{cell}}/T)/\partial(1/T)$ (mV)	$\Delta\bar{S}_{\text{Sr}}$ ($\text{J mol}^{-1} \text{K}^{-1}$)	$\Delta\bar{H}_{\text{Sr}}$ (kJ mol^{-1})
0.05	728-1007	157	883	30.3	-170.4
0.10	754-1009	69.2	919	13.4	-177.3
0.15	786-987	27.7	926	5.3	-178.7
0.20	835-987	6.4	913	1.2	-176.2
0.20	786-835	-570	1395	-110	-269.2
0.25	883-959	0.8	914	0.2	-176.4
0.25	782-883	-602	1469	-116	-283.5
0.30	908-984	-40.7	904	-7.9	-174.4
0.30	831-908	-611	1423	-118	-274.6
0.30	782-831	-133	1023	-25.7	-197.4
0.35	959-1010	-76.6	964	-14.8	-186.0
0.35	831-959	-527	1327	-101.7	-256.1
0.35	780-831	-181	1039	-34.9	-200.5
0.40	867-1010	-508	926	-98	-178.7
0.40	780-867	-62	1324	-12	-255.5
0.45	959-1010	-519	1197	-100.2	-231.0
0.45	780-959	-94.7	928	-18.3	-179.1
0.50	983-1009	-292	1111	-56.3	-214.4
0.50	779-983	-108	931	-20.8	-179.7
0.55	984-1009	-346	1167	-66.8	-225.2
0.55	779-984	-100	925	-19.3	-178.5
0.65	804-1007	-422	1169	-81.4	-225.6
0.75	933-1009	-2200	2725	-424.5	-525.8
0.75	830-933	-676	1265	-130.4	-244.1

Table 2. Measured emf, natural log of the activity of Sr in Bi, and the measured excess partial molar Gibbs energy of strontium of $x_{\text{Sr}} = 0.05$ to $x_{\text{Sr}} = 0.75$.

x_{Sr}	E (V)			$\ln a_{\text{Sr}}$			$\overline{G}_{\text{Sr}}^E$ (kJ mol ⁻¹)		
	788 K	888 K	988 K	788 K	888 K	988 K	788 K	888 K	988 K
0.05	1.008	1.024	1.039	-29.7	-26.8	-24.4	-175	-176	-176
0.10	0.976	0.982	0.989	-28.7	-25.7	-23.2	-173	-173	-172
0.15	0.948	0.951	0.953	-27.9	-24.9	-22.4	-170	-170	-168
0.20	0.946	0.919	0.920	-27.9	-24.0	-21.6	-172	-165	-164
0.25	0.946	0.891	0.891	-27.9	-23.3	-20.9	-174	-162	-160
0.30	0.919	0.881	0.864	-27.1	-23.0	-20.3	-170	-161	-157
0.35	0.912	0.879	0.838	-26.9	-23.0	-19.7	-169	-162	-153
0.40	0.878	0.880	0.829	-25.9	-23.0	-19.5	-164	-163	-153
0.45	0.879	0.870	0.826	-25.9	-22.7	-19.4	-164	-162	-153
0.50	0.845	0.834	0.822	-24.9	-21.8	-19.3	-159	-156	-153
0.55	0.845	0.835	0.824	-24.9	-21.8	-19.4	-159	-157	-154
0.65	0.843	0.801	0.758	-24.8	-20.9	-17.8	-160	-151	-143
0.75	0.836	0.769	0.610	-24.6	-20.1	-14.3	-159	-146	-115

Table 3. Reported crystal structures in Sr-Bi system [14–16].

Phase	x_{Sr}	Space group (Pearson symbol)	Density (mg m ⁻³)	Volume (nm ³)	Lattice parameters	
					(nm)	(°)
Bi	0.00	<i>hR6</i>	9.81	0.2123	a=0.45459	$\alpha=90$
		<i>R-3m</i>			b=0.45459	$\beta=90$
					c=1.18623	$\gamma=120$
SrBi ₃	0.25	<i>cP4</i>	9.26	0.12818	a=0.5042	$\alpha=90$
		<i>Pm-3m</i>			b=0.5042	$\beta=90$
					c=0.5042	$\gamma=90$
Sr ₂ Bi ₃	0.40	<i>oP20</i>	7.6	0.70069	a=1.5631	$\alpha=90$
		<i>Pnna</i>			b=0.6793	$\beta=90$
					c=0.6599	$\gamma=90$
Sr ₁₁ Bi ₁₀	0.52	<i>tI84</i>	6.76	2.9993	a=1.2765	$\alpha=90$
		<i>I4/mmm</i>			b=1.2765	$\beta=90$
					c=1.8407	$\gamma=90$
Sr ₄ Bi ₃	0.57	<i>cI28</i>	6.3	1.0306	a=1.0101	$\alpha=90$
		<i>I-43d</i>			b=1.0101	$\beta=90$
					c=1.0101	$\gamma=90$
Sr ₅ Bi ₃	0.63	<i>hP16</i>	5.77	0.61278	a=0.963	$\alpha=90$
		<i>P6₃/mcm</i>			b=0.963	$\beta=90$
					c=0.763	$\gamma=120$
Sr ₂ Bi	0.67	<i>tI12</i>	5.75	0.44377	a=0.501	$\alpha=90$
		<i>I4/mmm</i>			b=0.501	$\beta=90$
					c=1.768	$\gamma=90$
Sr (rt)	1.00	<i>cF4</i>	2.58	0.2253	a=0.60849	$\alpha=90$
		<i>Fm-3m</i>			b=0.60849	$\beta=90$
					c=0.60849	$\gamma=90$
Sr (ht)	1.00	<i>cI2</i>	2.55	0.1141	a=0.485	$\alpha=90$
		<i>Im-3m</i>			b=0.485	$\beta=90$
					c=0.485	$\gamma=90$

Table 4. Summary of transition temperatures determined by emf and DSC techniques.

x_{Sr}	T_{solidus} (K)		T_{liquidus} (K)	
	Emf	/ DSC	Emf	/ DSC
0.05	—	/ 543	706	/ —
0.10	—	/ 543	744	/ 745
0.15	—	/ 543	786	/ 786
0.20	—	/ 543	835	/ 833
0.25	—	/ 543	880	/ 873
0.30	841	/ 843	912	/ 917
0.35	843	/ —	955	/ —
0.40	908	/ —	—	/ —
0.45	908	/ —	—	/ —
0.50	979	/ —	—	/ —
0.55	984	/ —	—	/ —
0.75	929	/ —	—	/ —

Figure 1a

Figure 1b

Figure 1. Comparison of standard electrode potentials of selected alkaline/alkaline-earth elements, calculated using the standard free energies of formation of (a) pure fluorides and (b) pure chlorides at 873 K [12].

Figure 2a

Figure 2b

Figure 2. (a) Schematic electrochemical cell design from side and top views with approximate dimensions and (b) XRD spectra (normalized to the most intense peak for each spectrum) of $\text{CaF}_2\text{-SrF}_2$ electrolyte before and after the sintering, compared with pure (*) CaF_2 and SrF_2 diffraction patterns [14].

Figure 3a

Figure 3b

Figure 3. (a) Emf values and temperature measured as a function of time upon cooling and heating a Sr-Bi ($x_{\text{Sr}} = 0.10$)|CaF₂-SrF₂(s)|Sr(in Bi) cell with Sr-Bi alloys $x_{\text{Sr}} = 0.10, 0.15$, and 0.20 and (b) emf values as a function of temperature obtained from Sr(s)|CaF₂-SrF₂(s)|Sr-Bi($x_{\text{Sr}} = 0.10$).

Figure 4a

Figure 4b

Figure 4c

Figure 4. Emf values of various Sr-Bi alloys versus pure Sr, E_{cell} , as a function of temperature for (a) $x_{\text{Sr}} = 0.05$ to $x_{\text{Sr}} = 0.25$, (b) $x_{\text{Sr}} = 0.25$ to $x_{\text{Sr}} = 0.55$, and (c) $x_{\text{Sr}} = 0.50$ to $x_{\text{Sr}} = 0.75$.

Figure 5. Graphical representation of E_{cell}/T vs. $1/T$ to estimate the change in partial molar enthalpy of alloys $x_{\text{Sr}} = 0.05\text{--}0.15$, where the slope is $-\Delta\bar{H}_{\text{Sr}} / zF$ at each composition.

Figure 6a

Figure 6b

Figure 6c

Figure 6. (a) Measured emf values (E_{cell}), (b) natural log of activity of strontium ($\ln a_{\text{Sr}}$), and (c) excess partial molar Gibbs energy ($\bar{G}_{\text{Sr}}^E$) as a function of mole fraction x_{Sr} at 888 K.

Figure 7a

Figure 7b

Figure 7. X-ray diffraction patterns of Sr-Bi alloys (a) $x_{\text{Sr}} = 0.00$ to $x_{\text{Sr}} = 0.40$ and (b) $x_{\text{Sr}} = 0.40$ to $x_{\text{Sr}} = 1.00$, compared to the diffraction patterns of Sr-Bi intermetallic compounds (*) [14,15].

Figure 8. SEM image of $x_{\text{Sr}} = 0.25$ alloy that shows the presence of three distinct phases of Bi (bright), SrBi_3 (gray), and Sr_2Bi_3 (dark gray) based on the chemical analysis by EDS.

Figure 9. Differential scanning calorimetry data collected upon heating Sr-Bi alloys $x_{\text{Sr}} = 0.05$ to $x_{\text{Sr}} = 0.30$ at 7 K min^{-1} , indicating phase transitions of eutectic temperatures ($\circ$), liquidus temperatures (*), and solidus temperature ($\square$) for $x_{\text{Sr}} = 0.30$.

Figure 10. Comparison of experimentally determined phase behavior with the equilibrium phase diagram, adapted from the work by Wang *et al.* [17,18]. The phase transition temperatures were determined by emf measurement ($\circ$) and DSC technique ($\square$). The observed phases of Sr_2Bi_3 , and Sr_4Bi_3 are indicated by dashed lines. Reprinted with permission from Ref. [17]. Copyright 2014 Elsevier.