Experimentally Determined Phase Diagram for the Barium Sulfide-Copper(I) Sulfide System Above 873 K (600 °C)


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Experimentally Determined Phase Diagram for the Barium-sulfide – Copper (I) Sulfide System above 600°C

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Abstract

The phase diagram of the barium sulfide – copper(I) sulfide system was investigated above 873 K (600 °C) using a custom-built differential thermal analysis (DTA) apparatus. The melting point of barium sulfide was determined utilizing a floating zone furnace. Four new compounds, Ba2Cu14S9, Ba2Cu2S3, Ba3Cu6S7, and Ba6Cu2S10 were identified through quench experiments analyzed with wavelength dispersive x-ray spectroscopy (WDS) and energy dispersive x-ray analysis (EDS). A miscibility gap was observed between 72mol% and 92mol% BaS using both DTA experiments and in-situ melts observation in a floating zone furnace. A monotectic was observed at 94.5 mol% BaS and 1288 K (1015 °C).

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Introduction

Despite their relevance in earth science and materials engineering, high-temperature regions of sulfide phase diagrams – including binaries – are often missing or incomplete, in particular with respect to the stability of their molten phases. This omission is due in part to the experimental difficulty in handling those systems at high temperature, and in part to the challenges faced by current computation modeling practices in predicting solid/liquid equilibria for such systems. Indeed, binary sulfide systems can exhibit a variety of electronic properties across temperature and composition [1]. For example, chalcocite Cu$_2$S is a p-type semiconductor from room temperature to above its melting point, but will undergo metallization in the molten state above its melting point. Solid BaS, considered the most ionic of all alkaline earth sulfides, is presumably an n-type semiconductor with a band gap of 2.1eV [2], as validated from a study of its conductivity as a function of temperature [3]. With increasing concentration, sulfur can also offer a variety of bonding to the metal species leading to metal-like electronic properties [4] (see CuS) or formation of polysulfides (see alkaline sulfides for example [1]).

Due to the relative abundance of Ba and S, its low cost, and unique chemical nature [2], barium sulfide (BaS) is an important sulfide compound for which usage is hindered by a lack of thermodynamic understanding of its chemical interactions with other sulfides [5-9], including Cu$_2$S. Despite such uncertainty, its usage in combination in the solid-state with Cu$_2$S has been put forth for new high temperature superconductors [5] photovoltaic materials [10], or thermoelectrics [11,12]. Independently [13], the addition of barium sulfide to copper (I) sulfide (Cu$_2$S) at 56.8 mol% and 1379 K proved to form a possible electrolyte for liquid copper extraction via electrolysis, where the addition of BaS is thought to decrease the electronic conductivity of Cu$_2$S. Recent results [14] with addition of La$_2$S$_3$ to this composition ((BaS)$_{54}$-(Cu$_2$S)$_{31}$-(La$_2$S$_3$)$_{15}$) enabled the extraction of Mo, Re and Cu using direct electrolysis of such electrolyte with higher efficiency. The reason for such increase in efficiency has been attributed to the increased ionic nature of sulfides melts when the concentration in Cu$_2$S is lower.

The development of such new materials or processes requires a better description of the pseudo-binary BaS - Cu$_2$S, which itself requires new experimental methods. Indeed, the high temperature behavior of pure barium sulfide remains uncertain, with reported values for its melting point ranging from 1473 K to over 2473 K [9,15]. Consequently, most BaS-containing
pseudo binaries and higher order systems have been given little to no attention for concentration ranges rich in barium sulfide. Previously, the BaS-Cu$_2$S system has been investigated in the region from pure Cu$_2$S through 60 mol% BaS by Andreev et al [5]. Two compounds were observed using electronic spectroscopy and analysis, BaCu$_4$S$_3$ and BaCu$_2$S$_2$, in addition to a eutectic at 27 mol% BaS at a temperature of 908 K (635 °C). The liquidus line for compositions richer than 60 mol% BaS until pure BaS was suggested to be linear, a questionable assumption considering the uncertainty of the BaS melting point.

Here we report the first thermal stability study over the entire composition range of the BaS-Cu$_2$S system. Differential thermal analysis [16] (DTA) was used to identify transitions across the full extent of compositions from 873 K up to 1748 K. With the limited sensitivity of classical DTA systems [16] to accurately detect phase transitions in the BaS-rich region, a novel and easy-to-construct set-up was designed to maximize the ratio of the thermal arrest signals to background noise. DTA results were supplemented with quench experiments and visual observation of samples in a container-less floating zone furnace, enabling new measurement of the melting point of BaS and in-situ visualization of liquid phase separation for BaS-rich compositions. Results in the region from pure Cu$_2$S to 60 mol% BaS were in agreement with those of Andreev et al [5]. The region from 60 mol% BaS to pure BaS was found to contain a previously unreported miscibility gap from 72 mol% BaS to 92 mol% BaS and a monotectic at 94.5 mol% BaS at a temperature of 1288 K (1015 °C). Four previously unreported compounds were observed: Ba$_2$Cu$_{14}$S$_9$, Ba$_2$Cu$_2$S$_3$, Ba$_5$Cu$_4$S$_7$, and Ba$_9$Cu$_2$S$_{10}$.

Figure 1: Schematic of DTA apparatus
The DTA apparatus (Figure 1) was designed and fabricated in-house. The setup consisted of two thermopiles, a sample and a reference, enclosed in an alumina disk (22 mm in diameter, 10 mm in height). Each thermopile consisted of seven R-type thermocouples (RhPt\textsubscript{13}/Pt) each held in two-bore alumina tubes arranged in a hexagonal geometry – the fourteen total thermocouples being wired back and forth in series, alternating between the two thermopiles. The fourteen thermocouple geometry was adopted to maximize the thermal event signal strength in comparison to random background noise in order to facilitate the detection of first order and second order phase transitions, while retaining a geometry compact enough for the sample and reference to be held in the uniform hot zone of the tube furnace. The circular disk was secured by two alumina rods (220 mm in length, $\varnothing$3 mm) to a bottom disk (10 mm in height, $\varnothing$22 mm) to stabilize the setup. Alumina joints were held together using alumina or zirconia paste. Both alumina support rods protruded from the top disk by 10 mm, providing the means to attach an alumina sheath to hold the sample and reference in place. The bottom disk was supported by a four-bore alumina rod ($\varnothing$6.13 mm), which ran through a bottom compression fitting that held the DTA setup sealed in an alumina tube (Inner $\varnothing$23 mm, Outer $\varnothing$25 mm). Additional compression fitting at the top allowed for experiments to be run in an argon atmosphere (99.95% purity, Air Gas). Prior to a run, the system was purged with argon for 15 minutes at a flow rate of 15 cm$^3$.min$^{-1}$, then reduced to 5 cm$^3$.min$^{-1}$ during a run.

Thermocouple leads measuring the potential difference between the sample and reference compartment, as well as the temperature of the sample (measured from the thermocouple in the center of the sample thermopile) were ran down through the four-bore alumina rod. All exposed thermocouple wires were insulated using single-bore, thin-walled alumina tubes. Voltage and temperature data were collected using a 24bit data acquisition unit (National Instruments, NI USB-9162, NI-9211) at a data acquisition rate of 3 Hz. To ensure a clear background suitable for thermal signal identification, blank tests without any sample or reference were performed at heating rates of 5 and 10 K min$^{-1}$, from 293 K to 1473 K. The DTA apparatus was calibrated using the melting points of high purity zinc, aluminum, silver, and copper.

Samples were obtained from mixing barium sulfide (BaS, 99.9% pure metal basis, Sigma Aldrich) with copper (I) sulfide (Cu$_2$S, 99.5% pure metal basis, Alfa Aesar). All samples were
prepared in an argon glove box to prevent oxidation or hydration. Sample weights from 300 mg to 500 mg were used for DTA.

Samples were held in graphite crucibles sealed in either quartz or molybdenum ampoules. The graphite crucibles (Outer $\varnothing 6.1$ mm, Inner $\varnothing 5.5$ mm, bottom thickness of 0.2 mm) were machined in-house from isostatically pressed graphite (Tokai Carbon). Flat bottom quartz ampoules (Outer $\varnothing 9.5$ mm, Inner $\varnothing 7.0$ mm, bottom thickness of 0.5 mm) were made in-house. The graphite crucible was then placed into the quartz ampoule, the latter being heated under vacuum to a tight fit against the graphite crucible to ensure adequate thermal contact. After loading the graphite crucible with the sample and prior to vacuum sealing, quartz wool was forced down the quartz ampoule to clean the quartz tube of any powder. A quartz rod ($\varnothing 6.1$ mm) was placed into the quartz ampoule above the quartz wool. The ampoule was then purged with argon and evacuated to a pressure of 200Pa. The quartz ampoule was then vacuum formed and welded to the quartz rod to provide the seal.

Molybdenum ampoules (see Figure 2, Outer $\varnothing 9.5$ mm, Inner $\varnothing 6.13$ mm, 30 mm depth, bottom thickness of 1 mm) were machined in-house using a lathe equipped with carbide tools. The inner bottom of the ampoule was made flat using an end mill, while the outside bottom was ground flat using 80 grit, 320 grit, 600 grit, and 1200 grit silicon carbide sandpaper. The top 15 mm of the ampoule were internally threaded with a M8 x 1.25 tap. While in an argon glove box, the graphite crucible was filled with the sample, then pressed into the bottom of the ampoule. A flat cylindrical graphite plug ($\varnothing 6.13$ mm, 5 mm in height) was pressed onto the top of the graphite crucible in the ampoule. A M8 x 1.25 threaded molybdenum rod 15 mm in length was tightly screwed into the ampoule to secure the

**Figure 2: Molybdenum Ampoule Design**
graphite plug flush against the top of the graphite crucible. The atmospheric seal was created by the flat contact between the cap and the crucible top; the threaded rod served to press the cap tightly in place. For DTA experiments, alumina disks (Ø9.5 mm, 0.5 mm thick) were placed between the thermopiles and the molybdenum ampoules to avoid shorting the thermocouples.

For samples in quartz ampoules an empty graphite crucible was used as a reference. For samples in molybdenum ampoules, a molybdenum slug was used as a reference. References were prepared to have equal heat capacities with the sample to ensure a smooth background signal. The alumina tube containing the DTA apparatus and samples was placed vertically into a tube furnace (Lindberg/Blue, Mini-Mite) in order to locate the samples and thermocouple in its hot zone. Temperature was controlled using a PID process controller (Eurotherm, 2416). Heating rates between 1 and 20 K min\(^{-1}\) were investigated, with the optimal rate found to be 10 K min\(^{-1}\) and 300 mg for Cu\(_2\)S-rich compositions, and 4 K min\(^{-1}\) and 400 mg for BaS-rich samples. Each sample composition was subjected to three to five heating cycles, from 873 K to 100 K above the anticipated melting point, as determined from the liquidus slope. Temperature ramping was continuous and neither the maximum nor minimum temperatures were held for an extended duration. The first trace served to pre-melt the mixture. Subsequent heating traces showed signals with thermal arrests reproducible to ± 1 K. Only the heating traces were used to determine phase transition temperatures, as cooling traces showed significant undercooling.

The melting point of pure barium sulfide was estimated in a floating zone optical furnace. A barium sulfide rod (Ø12.5 mm) was prepared from barium sulfide (BaS, 99.7% metals basis, Alfa Aesar) by sintering at 1748 K for 1 hour in a molybdenum ampoule similar to those used for DTA measurements. The barium sulfide rod was suspended using a nickel wire in the hot zone of the furnace under argon at a pressure of 100,000 Pa, as the power was slowly increased at 1% per minute. The sample rod was observed using a video camera inside the furnace. When the tip of rod was observed to start melting, the power was held constant and the temperature at the tip was measured using a Type C (WRh\(_5\)/WRh\(_{26}\)) thermocouple. The melting point of a similar rod of composition 80 mol% BaS - 20 mol% Cu\(_2\)S was also measured.

Quench experiments were performed to identify previously unknown compounds as suggested by the appearance and disappearance of invariant signals. Graphite ampoules of a similar design to the molybdenum ampoules utilized for DTA were used. Samples of 45 mol%
BaS, 50 mol% BaS, and 55 mol% BaS were held at temperatures ranging from 1073 K to 1273 K prior to quenching. Samples of 60 mol% BaS were held at 1473 K for 2 hours, then held at 1073 K for 5 hours prior to quenching. Samples of 70 mol% BaS, and 80 mol% BaS were held for two hours at 1473 K and 1723 K respectively. Ice water, liquid nitrogen, or liquid gallium (room temperature) were used as quenching media. After quenching, the samples were placed in epoxy, cross-sectioned, and polished with kerosene using 600, 1200, 2400 and 4000 grit silicon carbide paper. The microstructure and elemental composition of the samples were then analyzed using scanning electron microscopy (SEM, JEOL JSM-6610LV, JEOL Ltd.) equipped with an energy dispersion spectroscopy analyzer (EDS, Sirius SD detector, SGX Sensortech Ltd.) and a wavelength dispersive x-ray analyzer (WDS) with a JEOL-JXA-8200 Superprobe (JEOL Ltd.) instrument operated at an accelerating voltage of 15 kV, a beam current of 20 nA, and a beam size of 1 μm. Pure copper and barium sulfate standards were used for calibration of the probe.

**Results**

*Differential Thermal Analysis*

The in-house designed and constructed DTA setup and ampoules performed accurately and consistently. The quartz ampoules were significantly easier to make than the molybdenum ampoules, but had several shortcomings. The thin bottom of the quartz ampoule necessitated that the sample be sealed under low pressure to avoid rupture at high temperatures due to gas expansion. At compositions greater than 65 mol% BaS however, the high vapor pressure of the sample coupled with such low internal pressure caused vaporization of the mixture which subsequently attacked the inside surface of the quartz ampoule, reacting with quartz, causing failure of the ampoule. Furthermore, thermal signals of phase transitions became more difficult to detect at higher BaS content, which was further hindered by insufficient heat transfer between the quartz ampoule and the thermocouples.
The molybdenum ampoules solved the problems encountered with barium sulfide rich samples. The enhanced heat transfer from the sample through the molybdenum ampoules to the thermocouples resulted in stronger peaks. The relatively high strength of molybdenum at elevated temperatures [17] allowed ampoules to be sealed under atmospheric pressure at room temperature. At elevated temperatures, argon pressure reached up to 500,000 Pa inside the crucibles, high enough to slow the kinetics of vaporization. The stability in pressure of the ampoule is long enough to reach the melting temperature before vaporization significantly shifts the sample composition. Simultaneously, the pressure is not too high as to have a measurable effect on the thermodynamic measurements of solid-state phase transition or liquidus measurements. Quartz ampoules were used for compositions up to 65 mol% BaS. Molybdenum ampoules were used for compositions ranging from 50 mol% to 95 mol% BaS. In the region

**Figure 3**: Variation of the thermopile voltage with temperature during heating of 80 mol% BaS-20 mol% Cu₂S and corresponding thermal arrests.
from 50 mol% to 65 mol% BaS, both molybdenum and quartz ampoules were utilized and showed good agreement in the obtained phase transition temperatures.

Thermal arrest signals were identified (see example of a trace in Figure 3) using the methods presented by Mackenzie [16], and are reported in Table 1. Liquidus data obtained from pure Cu$_2$S to 55 mol% BaS were in good agreement with prior publications [5]. The region from

**Figure 4**: Cross sections of ampoules illustrating phase separation
60 mol% BaS revealed several previously unknown features, distinctly different from the predictions from Andreev et al [5].

In compositions ranging from pure Cu$_2$S to 70 mol% BaS, cross-sections of the DTA ampoule showed the existence of one solidified, shiny, liquid (L1). In compositions ranging from 92 mol% BaS to pure BaS, the solidified liquid appeared less shiny, ionic-like solid (L2). In compositions ranging from 75 mol% to 90 mol% BaS, both solidified liquids were present (see Figure 4), indicating that the presence of a liquid miscibility gap.

**Floating Zone Tests**

The melting point of BaS was found to be 2508 K, in good agreement with previous high temperature readings, further corroborating the notion that the melting point of barium sulfide is highly susceptible to impurities, with lower reported values inherited from the presence of such impurities. Through the heating trace, minimal vaporization was observed before melting. Upon melting, the color of the barium sulfide changed from off-white to dark grey and the rate of vaporization observed with the camera increased.

Floating zone melting and in-situ video recordings (see Figure 5) at 80 mol% BaS showed the presence of two immiscible liquids – one that appeared reflective; and one that appeared dark and opaque. Upon melting, the sample was observed to phase separate, with the opaque liquid being at the bottom of the droplet (Figure 5). High rates of vaporization from the liquids prohibited heating of the sample above the critical point of the miscibility gap. Upon cooling, the opaque liquid (L2) was found to correspond to the ionic solid, while the reflective liquid (L1) was found to correspond to the shiny, metal-like solid observed in Figure 4 with DTA ampoules.
**Figure 5**: Liquid separation observed in the floating zone furnace for 80 mol% BaS, T~ 1375 K, 2 seconds, 10 seconds, and 20 seconds after melting

**Quench Experiments**

The appearance and disappearance of invariant signals predicted three new compounds – one at approximately 65 mol% BaS, one at approximately 72 mol% BaS, and a syntectic compound at approximately 90 mol% BaS. Quench experiments were utilized to verify the composition of these compounds. EDS and WDS analysis confirmed these compounds to be Ba$_2$Cu$_2$S$_3$, Ba$_5$Cu$_4$S$_7$, and Ba$_9$Cu$_2$S$_{10}$ respectively. The known compounds BaCu$_4$S$_3$ and BaCu$_2$S$_2$ were observed, as well as another new compound, Ba$_2$Cu$_{14}$S$_9$. Evidence of Ba$_2$Cu$_{14}$S$_9$ did not appear on any DTA signals, indicating that the compound decomposes below the minimum studied temperature of 873 K. The quench experiments performed on the 80 mol% BaS from 1723 K showed the existence of only one liquid, indicating that the critical point of the miscibility gap occurs in the temperature range studied by DTA.

**Discussion**

Based on the data collected through DTA, quench experiments, and floating zone tests, an updated phase diagram (Figure 6) is proposed for the pseudo binary Cu$_2$S-BaS. The points depicted correspond to the experimentally measured temperatures (Table 1), whereas the invariant temperatures correspond to the average transition temperature observed across the relevant composition range. A summary of the corresponding reactions can be found in Table 2, along with the average temperatures at which the reactions was observed. It is proposed to discuss our results in reference to the work by Andreev [5], which study also investigated temperature lower than 800K and reviewed the properties of the solid-state compounds found at that time. The Cu$_2$S-rich side phase boundaries proposed by Andreev [5] up to BaCu$_2$S$_2$ (50...
mol% BaS) are confirmed. A eutectic Cu$_2$S-BaCu$_4$S$_3$ at 27 mol% BaS is found at a temperature of 908 K with BaCu$_4$S$_3$ and BaCu$_2$S$_2$ disappearing peritectically at 933 and 1028K respectively. A polymorphic transformation of BaCu$_2$S$_2$ cited by Andreev [5] may be responsible for the unattributed invariant at 873K, though dedicated study would be necessary to validate this finding. More importantly for novel usage of BaS, the liquidus are found to be drastically lower than predicted by Andreev [5] in the region ranging from 55 mol% to 95 mol% BaS, and 3 new compounds (Ba$_2$Cu$_2$S$_3$, Ba$_5$Cu$_4$S$_7$, and Ba$_9$Cu$_2$S$_{10}$) and a miscibility gaps are found. The first compound (Ba$_2$Cu$_2$S$_3$, or 2BaS.Cu$_2$S, 66mol% BaS), forms as a peritectic from BaCu$_2$S$_2$ at 1028K and disappears peritectly at 1089K, suggesting that its synthesis from the melt will be difficult. It is indeed bounded by Ba$_5$Cu$_4$S$_7$ (5BaS.2Cu$_2$S, 72mol% BaS) above 1089K, itself stable until 1278K. Ba$_5$Cu$_4$S$_7$ is the last high temperature compound stable until the miscibility gap, disappearing peritectically to form the Cu$_2$S-rich liquid and Ba$_9$Cu$_2$S$_{10}$. Ba$_5$Cu$_4$S$_7$ is in principle a compound easily formed from a melt, thanks to its broad range of immiscibility in both composition (55 to 72% BaS) and temperature (around 200K).
Figure 6: Cu$_2$S - BaS phase diagram proposed from the experimental results of DTA, floating zone experiments, and quench experiments.

Ba$_9$Cu$_2$S$_{10}$ (9BaS.Cu$_2$S, 90mol% BaS) is the most stable compound found in this thermal study, responsible for the liquid-liquid immiscibility demonstrated by both quench DTA (Figure 4) and in-situ floating-zone (Figure 5) observations. The miscibility gap is observed from 72 mol% to 92 mol% BaS at a temperature of 1351 K. Its critical point was found at 82 mol% BaS at a temperature of 1469 K. Thanks to its mixing with a Cu$_2$S-rich liquid up to 1351K and a monotectic with 94.5 mol% BaS at a temperature of 1288 K, Ba$_9$Cu$_2$S$_{10}$ thermal stability enables liquids to be formed at very high BaS-content at more than a 1000K below BaS melting point.

The measurement of the melting point of BaS at 2508K is in agreement with a recent molecular dynamic estimation [18] but not with the data available in CRC handbook [15]. BaS is
not anticipated to undergo polymorphic transformations as a solid, and therefore the signals reported for compositions higher than 90\text{mol}\%\text{BaS} may reflect solid-state transformations from Ba$_6$Cu$_2$S$_{10}$. Other unattributed signals and phase transitions may be indication of other undiscovered compounds. Further research would be needed to verify these hypotheses.

The presence of a liquid miscibility gaps in ternary systems Cu-S-X is not entirely surprising, though to the best of the authors knowledge is the first time it is reported for X being an alkaline-earth element, here Ba. It is not anticipated with X being Ca or Mg according to other reports from Andreev [19]. It may however be that, as for BaS, a special experimental device is necessary to identify such miscibility gaps with those other alkaline-earth elements. Considering the large difference in electronic properties of the molten end members Cu$_2$S and BaS, operating in the miscibility gap may offer unconventional features for such materials systems. Indeed, the recent results attributing the presence of miscibility gaps in liquid semiconductors to electronic entropy/electronic transport properties differences [20,21] suggest the properties of the two liquids identified in this study – and seen in Figure 4 and 5 – will be drastically different. The BaS-rich, heavier, more ionic liquid would be a strong candidate for use in electrochemical applications requiring an ionically-conductive liquid, while the Cu$_2$S-rich, lighter liquid would have properties more similar to a molten semi-conductor. Such features are anticipated to enable novel processes that require both properties present in immiscible phases.

**Conclusion**

The transition temperatures of the binary system of BaS-Cu$_2$S above 873 K (600°C) were mapped using an in-house designed and constructed differential thermal analysis (DTA) setup and ampoules. A eutectic was observed at 27 \text{mol}\% barium sulfide at a temperature of 908 K (635 °C). A miscibility gap was observed from 72 \text{mol}\% barium sulfide to 92 \text{mol}\% barium sulfide, with a critical point at 82 \text{mol}\% barium sulfide at a temperature of 1469 K (1196 °C). A monotectic was observed at 94.5 \text{mol}\% barium sulfide. A floating zone optical furnace was utilized to determine the melting point of pure barium sulfide and observe phase separation in immiscible liquids. Quench experiments were utilized to determine the compositions of three previously unknown compounds, Ba$_2$Cu$_2$S$_3$, Ba$_5$Cu$_4$S$_7$, and Ba$_6$Cu$_2$S$_{10}$, predicted through DTA, as well as a fourth compound, Ba$_2$Cu$_{14}$S$_9$, existing below the temperature range studied.
Acknowledgements

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References


Figures:

**Figure 1**: Schematic of DTA apparatus

**Figure 2**: Molybdenum Ampoule Design

**Figure 3**: Variation of the thermopile voltage with temperature during heating of 80 mol% BaS-20 mol% Cu₂S and corresponding thermal arrests

**Figure 4**: Cross sections of ampoules illustrating phase separation

**Figure 5**: Liquid separation observed in the floating zone furnace for 80 mol% BaS, T~ 1375 K, at 2, 10, and 20 seconds after melting

**Figure 6**: Cu₂S - BaS phase diagram proposed from the results of DTA, floating zone, and quench experiments

**Table 1**: Thermal signals observed in the Cu₂S- BaS system

<table>
<thead>
<tr>
<th>Composition, mol% BaS</th>
<th>Liquidus Temperature, ( T_{\text{liq}} / ) K</th>
<th>Invariant Signals, ( T_{\text{inv}} / ) K</th>
<th>Non-Attributed Signals, ( T_{\text{non-attr}} / ) K</th>
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Table 2: Reactions observed in the Cu₂S- BaS system

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<th>Reaction</th>
<th>Reaction Temperature, T/K</th>
<th>Reaction Type</th>
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<td>L + Ba₂Cu₂S₃ = BaCu₂S₂</td>
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<td>L + Ba₅Cu₄S₇ = Ba₂Cu₂S₃</td>
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