

The Ba-Cu (Barium-Copper) System

137.33

63.546

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The assessed Cu-Ba equilibrium diagram in Fig. 1 has been derived from the works of Braun and Meijering [59Bra] and Bruzzone [71Bru]. Cu and Ba are virtually insoluble in one another in the solid state, but are soluble in all proportions in the liquid. Two intermediate phases of stoichiometry, Cu_{13}Ba and CuBa , are formed in this system, one of which (CuBa) undergoes congruent melting. A peritectic and two eutectic transformations are associated with these phases. The crystal structure of Cu_{13}Ba is isotypic with NaZn_{13} , whereas CuBa is the prototype of a new structure. No reports of thermodynamic properties of Cu-Ba alloys are available.

Equilibrium Diagram

The equilibrium phases listed in Table 1 in the Cu-Ba system are: (1) the liquid, miscible in all proportions and

stable down to 458 °C at 79.4 at.% Ba; (2) (Cu), the fcc solid solution based on Cu, with negligible solubility of Ba; (3) (Ba), the bcc solid solution based on Ba, with negligible solubility of Cu; (4) Cu_{13}Ba , the fcc intermediate phase that decomposes incongruently via a peritectic transformation at 670 °C; and (5) CuBa , the hexagonal intermediate phase that undergoes congruent melting at ~570 °C.

The lower temperature limits of stability of Cu_{13}Ba and CuBa have not been determined experimentally.

Ba is extremely reactive in air, and Ba-Cu alloys behave likewise. Thus, a contamination problem always exists with these alloys, particularly in the liquid. Both Braun and Meijering [59Bra] and Bruzzone [71Bru] prepared the alloys under argon atmosphere. Melting was carried out in Al_2O_3 crucibles by [59Bra], whereas [71Bru] used Fe crucibles for alloys above 60 at.% Ba and Mo crucibles

Fig. 1. Assessed Cu-Ba Phase Diagram

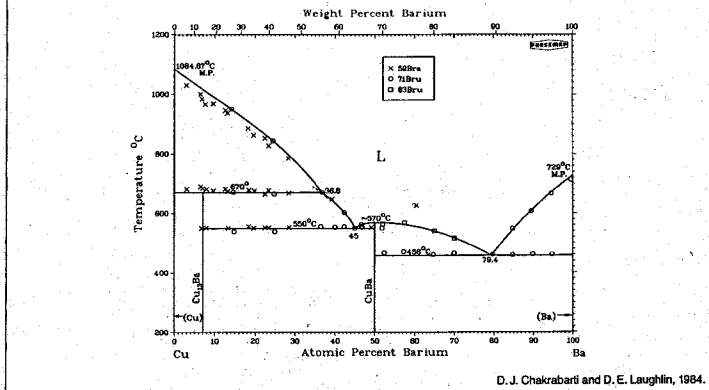


Table 1 Cu-Ba Crystal Structure and Lattice Parameter Data

Phase	Approximate composition range(a), at.% Ba	Pearson symbol	Space group	Prototype	Lattice parameters, nm		Reference
					a	c	
(Cu)	0	cF4	Fm3m	Cu	0.36147(b)	...	[Landolt-Börnstein]
Cu ₂ Ba	7.143	cF112	Fm3c	NaZn ₁₃	1.1754 ± 2(c)	...	[71Bru]
CuBa	50	hP8	P6 ₃ /mmc	BaCu	0.4499(c)	1.625	[80For]
(Ba)	100	cI2	Im3m	W	0.5013 ± 5(d)	...	[56Hir]
Pressure-stabilized phase							
Ba	100	hP2	P6 ₃ /mmc	Mg	0.3901(e)	0.6155	[63Bru]

(a) From the phase diagram. (b) At 18 °C, on elemental Cu. (c) On single crystals. (d) On elemental Ba of 99.3 wt.% purity at 25 °C. Structure is reported to be stable down to 5 K, having the lattice parameter 0.5000 nm; the same at RT is 0.501 nm [56Bar]. (e) At 62 kbar.

for Cu-rich compositions. The purity of the Cu and Ba used by [59Bra] was not specified, apart from the mention of the use of OFHC Cu. The results of the spectrographic analysis of samples with ~52 at.% Ba indicated a total impurity content in the alloy in excess of 1 wt.% (0.5 Sr, 0.3 Ca, 0.08 Fe, 0.04 Si, 0.06 N, 0.05 Mg, 0.01 Pb, and 0.002 Mn, in wt.%), which is equivalent to ~3 at.%. Thus, the purity of Ba used was perhaps between 94 and 95 at.%. [71Bru] used Cu of 99.999% and commercial grade Ba of 99.7% purity [63Bru]. The melting point of Ba (710 °C) reported in [71Bru] is, however, considerably below the accepted value of 729 °C [81BAP] and presumably resulted from impurity effects. Although some pickup of impurities during specimen preparation is also likely, the purity of the starting materials was either very low [59Bra] or not quite adequate [71Bru]. Thus, even if the overall features of the reported phase diagram are correct, the temperature and composition values of the phase boundaries may need some revision.

Both [59Bra] and [71Bru] used thermal analysis for determining the liquidus and the temperature invariant boundaries, and X-ray diffraction for determining the crystal structure and the solubility limits of the phases. The thermal analysis was conducted by both these investigators during cooling. The melts, however, were stirred only prior to cooling.

[59Bra] used direct thermal analysis and a somewhat higher cooling rate of about 7 °C/min, whereas [71Bru] used differential thermal analysis and a cooling rate of 2 to 4 °C/min (on a 2 g sample), with a reported temperature accuracy of ±1 °C. Compositions were determined by chemical analysis.

Liquidus and Solidus. [59Bra] extensively studied the Cu-rich portion of the diagram up to ~50 at.% Ba. [71Bru] extended the work across the entire diagram. There is reasonable agreement between these works in the overlapped region. However, the liquidus data of

Table 2 Invariant and Congruent Transformations in the Cu-Ba System

Reaction	Compositions(a), at.% Ba			Temperature, °C	Type
L + (Cu) \rightleftharpoons Cu ₁₃ Ba	36.8	~0	7.14	670	Peritectic
L \rightleftharpoons Cu ₁₃ Ba + CuBa	45	7.14	50	550	Eutectic
L \rightleftharpoons CuBa	50	50		~670	Congruent
L \rightleftharpoons CuBa + (Ba)	79.4	50	~100	458	Eutectic

(a) Compositions for the phases are given in the order they appear in column 1.

[59Bra] are generally lower and show greater scatter, presumably in consequence of the higher rate of cooling used in this work. The accepted liquidus, therefore, has been based primarily on the data of [71Bru] and has been drawn by a smooth curve that joins with the melting point of Cu at 1084.87 °C, according to [81BAP] (see Fig. 1). The limiting slope of the resulting liquidus ($\Delta T/X_{Ba}^L$) at Cu, approximately -11.7 °C/at.% Ba, agrees with the value of the theoretical maximum limiting slope of -11.74 °C/at.% solute, corresponding to the condition of zero solute solubility in Cu. The calculation has used the enthalpy of fusion and the melting point of Cu and has been based on the assumption that Raoult's law is satisfied by Cu in the liquid. The absence of any measurable difference in the lattice parameter values between pure Cu and the (Cu) phase in the Cu-Ba alloys, combined with the observation of two-phase fields in the 0.1 wt.% Ba-Cu alloy as observed metallographically by [59Bra], indicate that Ba has very little solid solubility in Cu. Thus, the initial slope of the liquidus at Cu is thermodynamically consistent with the experimental phase diagram. Above ~40 at.% Ba, the liquidus has been drawn based on the only available results due to [71Bru], except near pure Ba, where it is modified to connect to the accepted melting point of Ba at 729 °C, according to the compilations in [81BAP].

Although experimental data are not available close to pure Ba, the liquidus drawn by interpolation of data points from the nondilute regions has been used to estimate the initial slope of the liquidus at Ba, which is found to be approximately -10.6 °C/at.% Cu. Using the Van't Hoff relation, the corresponding initial slope ($\Delta T/X_{Ba}^L$) of the solidus (calculated from the enthalpy of fusion and the melting point of Ba, assuming Raoult's law has been satisfied by the solvent in both the liquid and the solid (Ba) phase) has been found to be -500 °C/at.% Cu. This indicates very little solid solubility of Cu in Ba, a conclusion that is consistent with the suggested lack of any solid solubility field in (Ba), according to [71Bru]. Thus, the estimated limiting slope of the liquidus at Ba is thermodynamically consistent with the absence of any significant solubility of Cu in (Ba). (The liquidus, as drawn by [71Bru] and connected to Ba at 710 °C, would have required an observable solubility of Cu in (Ba).)

From the occurrence of primary thermal arrests, three temperature-invariant incongruent-transformation lines have been identified in this system (see Table 2). However, because the measurements were done during cooling, undercooling effects are possible, so that the actual transformation temperatures may be somewhat higher. [59Bra] identified the two temperature invariants at 675 and 550 °C, corresponding to the peritectic

Table 3 Thermodynamic Properties of Phases of the Cu-Ba System(a)

Lattice stability parameters of Cu and Ba (Hultgren)

$$\begin{aligned} G_{Cu}^L &= 0 \\ G_{Ba}^L &= 0 \\ G_{CuBa}^L &= -13054 + 9.613T \\ G_{CuBa}^S &= -7748.8 + 7.732T \end{aligned}$$

Gibbs energy values from modeled parameters

$$\begin{aligned} G_{CuBa}^{CuBa} &= -16940 + 13.28T \\ G_{CuBa}^{CuBa} &= -30230 + 27.43T \\ G^L &= X(1-X)(-43978.5 - 2286X + 42.86T) \\ &\quad + RT[X \ln X + (1-X) \ln(1-X)] \end{aligned}$$

where X is atomic fraction of Ba.

Note: Moles for Cu₁₃Ba and CuBa refer to the respective atoms as elementary entities.

(a) From the phase diagram. All variables are expressed in J/mol and J/mol·K.

and eutectic transformations, respectively. The corresponding values reported by [71Bru] were 670 and 550 °C. In addition, he determined a third temperature invariant at 458 °C, corresponding to a eutectic transformation. The thermal arrest data of [59Bra] at 675 °C showed a scatter of nearly ± 15 °C, that may be related to the inherent difficulty in attaining equilibrium in a peritectic reaction. This was aggravated further by the faster rate of cooling during the thermal analysis of these alloys. By contrast, the data by the same authors showed little scatter at 550 °C, presumably because of the comparative ease in attaining equilibrium in a eutectic reaction. Considering that neither of the authors utilized stirring of the liquid during cooling to facilitate equilibration, the extent of scatter in the primary arrest data for the peritectic reaction does not appear too high.

The transformation temperatures accepted in this evaluation are 670 °C for the peritectic from [71Bru], 550 °C for the eutectic according to both [59Bra] and [71Bru], and 458 °C for the eutectic from [71Bru]. The compositions for the eutectic points at 45 and 79 at.% Ba, as given by [71Bru], are, at best, approximate, because no thermal analysis exists for alloys of these compositions, and no metallographic work was reported near these compositions. The same compositions, calculated in this evaluation from the thermodynamic variables in Table 3 (see Thermodynamics section and Table 4), have been found to be 45.0 and 79.4 at.% Ba, respectively. These are close to the values given by [71Bru] and have been accepted. The composition of the liquidus at 670 °C has been accepted at 36.8 at.% Ba, on the basis of the thermal arrest data of [71Bru].

Intermediate Phases. An intermediate phase of composition near Cu₁₃Ba was identified by [59Bra], from the arrest times in the thermal analysis of the liquid and from the determination of the chemical composition and the density of the phase that was isolated from the bulk by preferential dissolution in water. X-ray investigation by the authors on specimens with less than 49 at.% Ba confirmed the structure to correspond to the stoichiometry Cu₁₃Ba, whereas the invariance of the lattice parameter suggested the absence of any measurable phase field. Thus, Cu₁₃Ba is an intermediate phase with limited solubility and is formed peritectically from the liquid of 36.8 at.% Ba and the (Cu) phase at 670 °C.

Table 4 Experimental vs Calculated Liquidus for the Cu-Ba System

Experimental liquidus		Reference(a)	Calculated liquidus [this work]	
Temperature, °C	Composition, at.% Ba		Temperature(b), °C	Composition(c), at.% Ba
L/L + (Cu) boundary			L/L + (Cu) boundary	
1084.87	0	[81BAP]	1084.5	...
1075	0.75		1076.9	0.7
1050	3.5		1050.4	3.0
1025	6.1		1025.4	5.4
1000	8.8		1000.5	8.0
950	14.1		951.3	13.4
945	14.8	[71Bru](d)	944.7	...
900	19.3		900.4	18.9
850	24		849.5	23.9
842	24.7	[71Bru]	841.4	...
800	28		800.9	28.3
782(e)	28.5	[59Bra]	794.4	...
750	31.7		750.2	32.0
700	35		699.5	35.1
670	36.8	[71Bru]	669.3	36.7
L/L + Cu₁₃Ba boundary			L/L + Cu₁₃Ba boundary	
650	38.7		648.6	38.4
645(e)	39.5	[59Bra]		
610	41.6		609.8	41.4
600	42.4	[71Bru]	598.0	...
570	44.2		568.7	43.9
550	45		554.6	45.0
L/L + CuBa boundary			L/L + CuBa boundary	
570	50		568.1	...
565	49		565.9	...
560	46.8	[71Bru]		
560	56.7		558.9	59.6
550	62.5		551.7	63.5
530	67.5		528.7	68.6
515	70	[71Bru]	515.0	71.4
490	74		491.3	75.2
470	77.5		469.7	77.7
458	79.5		458.0	79.4
L/L + (Ba) boundary			L/L + (Ba) boundary	
729	100	[81BAP]	729.6	...
700	97.75		701.3	97.3
669	95	[71Bru]	670.9	...
650	93.4		649.8	92.9
605	89.8	[71Bru]	607.3	...
600	89.2		600.0	88.8
550	85.3		550.0	85.1
543	84.7	[71Bru]	541.8	...
500	81.8		499.0	81.8
458	79		458.7	79.37

(a) Experimental liquidus data without any indicated reference correspond to values obtained from graph by interpolation of experimental data. (b) These calculated temperatures have been determined using the analytic expressions in Eq 1 to 4, using the experimental compositions given in column 2 of this table. (c) These calculated compositions have been determined using the thermodynamic variables given in Table 3, at the temperatures given in column 1 of this table. (d) Data from [71Bru] are given as transcribed from the author's figure. (e) Datum deviates from the accepted liquidus value.

[71Bru] confirmed the occurrence of the Cu₁₃Ba phase and indicated the occurrence of yet another nearly stoichiometric phase below 570 °C, postulated earlier by [59Bra], having the composition CuBa. This was based on thermal analysis supported by X-ray structure determination studies.

The temperature of the congruent melting of CuBa at 570 °C, according to [71Bru], is tentative, because it was based on interpolation from nearby data, and no measurement exists at this composition. The experimental liquidus and solidus data, as transcribed from the figures of [71Bru] and [59Bra] and on which the assessed Cu-Ba equilibrium diagram in Fig. 1 has been based, is pre-

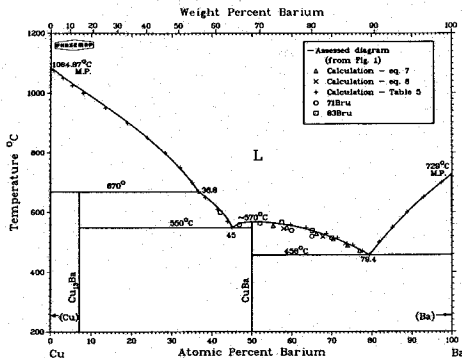
sented in Table 4. Tabulated thermal analysis results of [71Bru] are presented in Table 5 (see [83Bru]).

Analytic representations as polynomials of composition of the liquidus (temperature) have been obtained by least-square analysis over the different composition ranges. These are shown in Eq 1 to 4, below. The fit between the assessed and the calculated liquidus is within ± 2 °C in most of the ranges, as can be seen in Fig. 2 and in Table 4.

0 to 36.8 at.% Ba:

$$T = 1084.87 - 1016.3X + 1018X^2 - 3592X^3 \quad (\text{Eq 1})$$

Fig. 2 Calculated vs Experimental Phase Diagram for the Cu-Ba System



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Table 5 Thermal Analysis Results of Cu-Ba Alloys

Specimen composition, at.% Ba	Melting temperature, °C	Secondary arrest temperatures, °C		
		(Cu)/Cu ₁₃ Ba/L	Cu ₁₃ Ba/L/CuBa	CuBa/L/(Ba)
0	1084
15	950	670	540	...
25	845	662	536	...
52	565	...	550	...
57.5	567	470
65	540	458
70	515	463
80	458	458
85	545	456
90	605	458
95	665	457
100	710

From data of [83Bru, 71Bru].

36.8 to 45 at.% Ba:

$$T = 984.4 - 534.5X - 3130X^2 + 11910X^3 - 15626X^4 \quad (\text{Eq 2})$$

45 to 79.4 at.% Ba:

$$T = -755.9 + 6054X - 8704X^2 + 3785X^3 \quad (\text{Eq 3})$$

79.4 to 100 at.% Ba:

$$T = 726.0 - 1297(1 - X) + 1978(1 - X)^2 - 9961(1 - X)^3 \quad (\text{Eq 4})$$

Metastable Phases

There is no report of any metastable phase in this system.

Crystal Structures and Lattice Parameters

The crystal structures and the accepted lattice parameters of Cu, Ba, and the intermediate phases Cu₁₃Ba and CuBa are presented in Table 1.

The crystal structure of Cu₁₃Ba was determined by Braun and Meijering [59Bra] from powder and rotation X-ray photographs of the phase isolated from the bulk. The structure was identified to be isotypic with the NaZn₁₃ phase, and the corresponding lattice parameter was found to be 1.1719 nm. Bruzzone [71Bru] further refined the lattice parameter value (see Table 1) using single crystal samples grown from 16 to 25 at.% Ba alloy by cooling from the melt and preserving under an inert atmosphere.

[71Bru] also studied the single crystals of CuBa using rotation and Weissenberg X-ray photographs. The space group was identified from the Laue symmetry and extinctions to be $P6_3/mmc$, and the calculated lattice parameter values based on hexagonal symmetry were given as $a = 0.4495 \pm 0.0003$ nm and $c = 1.620 \pm 0.0003$ nm. The crystal structure of CuBa was solved by Fornasini and Merlo (80For), using single crystals of the stoichiometric phase made from 99.5 wt.% Ba and 99.999 wt.% Cu. The X-ray analysis was carried out by Laue, Weissenberg and precession methods. The lattice parameter values presented in Table 1 have been obtained from rotation patterns. CuBa has been found to have hexagonal symmetry, with slabs of trigonal prisms of Ba (with Cu atoms in their center) stacked in a close-packed manner along [001]. The weak Ba-Ba bonds between the adjacent slabs make CuBa behave as a layered phase.

The bcc structure of Ba was found to be stable down to 5 K [56Bar]. It undergoes allotropic transformations to cph under pressure [63Bar] above 53.3 kbar [66Jef].

Thermodynamics

No thermodynamic data are available on Cu-Ba alloys. Because the Cu-Ba phase diagram is reasonably well established, the equilibrium boundaries between the coexisting phases can be utilized to derive expressions for the thermodynamic variables of the different phases. The variables, in turn, can be used to reproduce the phase boundaries as a check for self-consistency and also to calculate the critical points in the system for which no experimental data may be available. Both of these aspects have been attempted in this evaluation in accordance with the following approach.

Because both the (Cu) and the (Ba) phases display virtually zero solubility, they have been assumed to be line phases, and the representation of their molar free energies has been obtained from the respective lattice stability parameter values for the solid/liquid transitions as given in [Hultgren]. The resultant expressions, relative to pure liquid Cu and pure liquid Ba as standard states (used throughout the calculations), are presented in Table 3.

The liquidus boundaries between 1084.87 and 670 °C and between 729 and 458 °C have been utilized to estimate the integral molar excess free energy expressions for the liquid. The latter has been expressed as a polynomial with composition in the following form:

$${}^E\Delta G^L = X(1-X) \sum_{i=1}^N (a_i^N \cdot X^{i-1} - T \cdot b_i^S \cdot X^{i-1}) \quad (\text{Eq } 5)$$

where a_i^N and b_i^S are, respectively, the coefficients for the enthalpy ($\Delta H/X(1-X)$) and entropy (${}^E\Delta S/X(1-X)$) functions of the liquid, and X is the atomic fraction of Ba. Both coefficients have been assumed to be independent of temperature. The simultaneous linear equations set up from the equilibrium relations between the liquid and the solid phases at several temperatures have been solved by the standard multiple least-squares regression analysis Gauss-Jordan reduction algorithm) to derive the values of the coefficients, a_i^N and b_i^S . In the present instance, use of 16 data points, eight on each side of the liquidus, and a combination of two coefficients of a_i^N and one of b_i^S , was found sufficient to represent the thermodynamic expression for the liquid that satisfactorily reproduces the phase

diagram. The number of the a_i^N and b_i^S terms was limited to a minimum in these calculations, as a compromise between the reproducibility of the calculated diagram, that improves with their increased numbers, and the simplicity of the model. The resultant expression for the ${}^E\Delta G^L$ is as follows:

$${}^E\Delta G^L = X(1-X)(-43979 - 2286X + 42.86T) \quad (\text{J/mol}) \quad (\text{Eq } 6)$$

The maximum value of ΔH according to Eq 2, corresponding to $X = 0.51$, is -11282 J/mol, and the corresponding ΔG value estimated at 1000 K is -6332 J/mol.

From a knowledge of the molar free energy of the liquid, the molar free energy of the Cu_{13}Ba phase, expressed in the form $(A + BT)$, has been estimated by considering equilibrium of the compound with the liquid at two temperatures, namely 670 and 550 °C, corresponding to the liquid compositions of 36.8 and 45 at.% Ba, respectively. In a similar manner, the molar free energy of CuBa has been estimated from the liquid at 570 (congruent point) and 458 °C (eutectic point), corresponding to the liquid compositions of 50 and 79 at.% Ba, respectively. The results for both phases are presented in Table 3.

The liquidus (composition), calculated at selected temperatures based on these derived expressions above and the lattice stability parameters for Cu and Ba, is shown in Fig. 2 and is tabulated in Table 4 for quantitative comparison with the experimental liquidus. The agreement between the liquidus results appears to be excellent.

Interestingly, the calculated liquidus coexisting with CuBa originally showed a disagreement with the liquidus data of [71Bru], being displaced above the latter, which indicated a possible undercooling effect. However, recent data from [83Bru] showed close agreement with the calculated liquidus (see Fig. 2 and Table 5), lending credence to the calculations made in this evaluation and to the modeling parameters derived for the different phases.

Figure 2 also shows the calculated (liquidus) data corresponding to two alternate expressions for the molar free energy of CuBa. In the one instance, the ΔG^{CuBa} was derived from the least-squares fit of liquidus data at four temperatures (570, 550, 520, and 458 °C), as shown in Eq 7. In the other instance, the data at 550 and 458 °C were used to derive the ΔG^{CuBa} , as in Eq 8.

$$\Delta G^{\text{CuBa}} = -30820 + 28.47T \quad (\text{J/mol}) \quad (\text{Eq } 7)$$

$$\Delta G^{\text{CuBa}} = -33300 + 31.68T \quad (\text{J/mol}) \quad (\text{Eq } 8)$$

The liquidus calculated from both Eq 7 and 8 is displaced below the experimental liquidus according to [83Bru], but this is not possible because the latter was determined by cooling. Therefore, the ΔG^{CuBa} expression presented in Table 3 is the most consistent with the experimental phase diagram.

The mutual stability of Cu_{13}Ba and CuBa, with respect to the (Cu) and (Ba) phases at lower temperatures, has been examined by considering the relative changes with temperature of the molar free energy of the four phases. The hypothetical decomposition temperatures for Cu_{13}Ba and CuBa occurred (in the metastable range)

above their formation temperatures, i.e., at 1014 and 775 °C, respectively. Thus, these phases are stable at all temperatures below their formation temperatures.

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*Indicates key paper.

#Indicates presence of a phase diagram.

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