Ag – Ba (Silver – Barium)

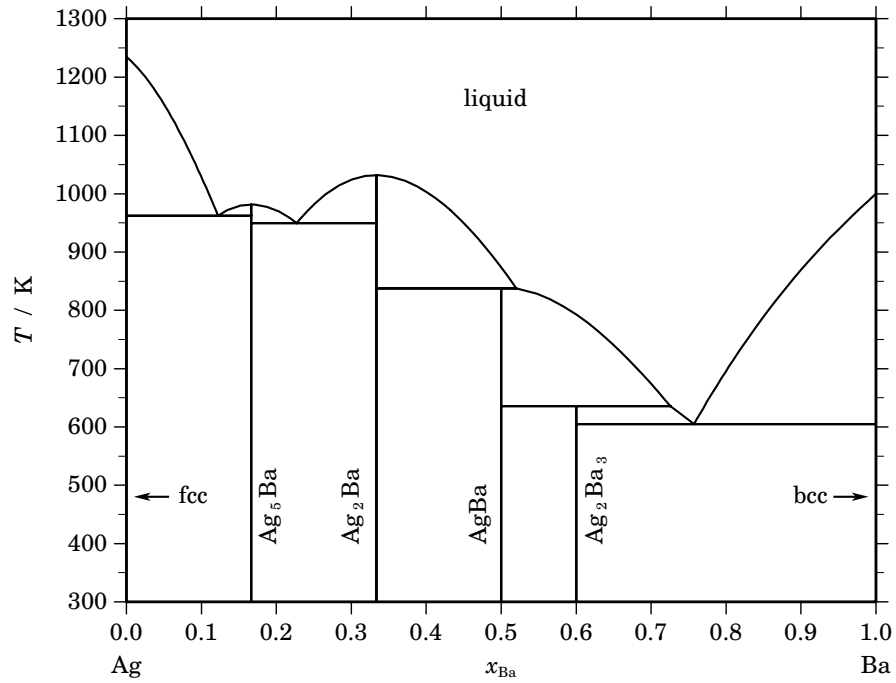

Fig. 1. Calculated phase diagram for the system Ag-Ba.

The Ag-Ba binary system contains two components interesting in the nuclear field, silver being part of AIC control rods (Ag-In-Cd). The phase diagram reported in the compilation of Okamoto [1992Oka] is mainly based on the experimental work of Bruzzone *et al.* [1987Bru] using DTA, X-ray and metallography. The older work of Weibke [1930Wei] using DTA has been discarded. Four intermetallic phases have been identified: Ag_5Ba, with a wide non-stoichiometry range, and three stoichiometric compounds, Ag_2Ba, AgBa, and Ag_2Ba_3. The first two melt congruently at 988 K and 1043 K, the two others decompose peritectically at 833 K and 633 K. There are two eutectic reactions located at 973 K on the silver side and at 513 K on the barium side. There is no reported mutual solubility of both elements in the solid state, and a complete miscibility in the liquid state. The enthalpy of mixing of liquid alloys of silver with barium and rare earth metals (La, Ce, Sm, Eu, Gd, Dy and Yb) have been measured by Ivanov and Witusiewicz [1992Iva] using isoperibolic calorimetry. No experimental data are available for thermodynamic properties of the intermetallic solid phases. This system was assessed by Chevalier and Fischer [1995Che]. The excess Gibbs energy of the liquid and the Gibbs energy of the intermetallic compounds which are all treated as stoichiometric were optimised from selected data for the phase diagram [1987Bru] and the enthalpy of mixing in the melt [1992Iva]. A sub-regular substitution model was used for the liquid. The heat capacity versus temperature and the entropy at 298.15 K of the compounds were estimated from the pure elements by using the Neumann-Kopp rule. The enthalpy of formation was optimised in consistency with other data. The calculations are in very satisfactory agreement with the selected experimental data.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Ag,Ba)_1$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	Ag_1
Ag_5Ba	$D2_d$	$CaCu_5$	$hP6$	$P6/mmm$	AG5BA	Ag_5Ba_1
Ag_2Ba	$\cdots$	$CeCu_2$	$oI12$	$Imma$	AG2BA	Ag_2Ba_1
AgBa	$B27$	FeB	$oP8$	$Pnma$	AGBA	Ag_1Ba_1
Ag_2Ba_3	$\cdots$	Er_3Ni_2	$hR45$	$R\overline{3}$	AG2BA3	Ag_2Ba_3
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	Ba_1

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Ba}			$\Delta_r H$ / (J/mol)
liquid $\rightleftharpoons$ Ag_2Ba	congruent	1031.9	0.333	0.333		−14037
liquid $\rightleftharpoons$ Ag_5Ba	congruent	981.7	0.167	0.167		−12181
liquid $\rightleftharpoons$ fcc + Ag_5Ba	eutectic	962.0	0.122	0.000	0.167	−11382
liquid $\rightleftharpoons$ Ag_5Ba + Ag_2Ba	eutectic	949.7	0.227	0.167	0.333	−12377
Ag_2Ba + liquid $\rightleftharpoons$ AgBa	peritectic	837.6	0.333	0.520	0.500	−10493
AgBa + liquid $\rightleftharpoons$ Ag_2Ba_3	peritectic	635.8	0.500	0.726	0.600	−3753
liquid $\rightleftharpoons$ Ag_2Ba_3 + bcc	eutectic	604.8	0.757	0.600	1.000	−7906

Table IIIa. Integral quantities for the liquid phase at 1273 K.

x_{Ba}	ΔG_m [J/mol]	ΔH_m [J/mol]	ΔS_m [J/(mol·K)]	G_m^E [J/mol]	S_m^E [J/(mol·K)]	ΔC_P [J/(mol·K)]
0.000	0	0	0.000	0	0.000	0.000
0.100	−9744	−6304	2.703	−6304	0.000	0.000
0.200	−16034	−10738	4.161	−10738	0.000	0.000
0.300	−19944	−13478	5.079	−13478	0.000	0.000
0.400	−21824	−14701	5.596	−14701	0.000	0.000
0.500	−21918	−14581	5.763	−14581	0.000	0.000
0.600	−20418	−13295	5.596	−13295	0.000	0.000
0.700	−17484	−11018	5.079	−11018	0.000	0.000
0.800	−13223	−7926	4.161	−7926	0.000	0.000
0.900	−7636	−4195	2.703	−4195	0.000	0.000
1.000	0	0	0.000	0	0.000	0.000

Reference states: Ag(liquid), Ba(liquid)

Table IIIb. Partial quantities for Ag in the liquid phase at 1273 K.

x_{Ag}	ΔG_{Ag} [J/mol]	ΔH_{Ag} [J/mol]	ΔS_{Ag} [J/(mol·K)]	G^E_{Ag} [J/mol]	S^E_{Ag} [J/(mol·K)]	a_{Ag}	γ_{Ag}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−2079	−964	0.876	−964	0.000	0.822	0.913
0.800	−5983	−3622	1.855	−3622	0.000	0.568	0.710
0.700	−11397	−7621	2.966	−7621	0.000	0.341	0.487
0.600	−18019	−12612	4.247	−12612	0.000	0.182	0.304
0.500	−25579	−18242	5.763	−18242	0.000	0.089	0.178
0.400	−33858	−24160	7.619	−24160	0.000	0.041	0.102
0.300	−42757	−30014	10.010	−30014	0.000	0.018	0.059
0.200	−52488	−35453	13.382	−35453	0.000	0.007	0.035
0.100	−64497	−40126	19.145	−40126	0.000	0.002	0.023
0.000	−∞	−43680	∞	−43680	0.000	0.000	0.016

Reference state: Ag(liquid)

Table IIIc. Partial quantities for Ba in the liquid phase at 1273 K.

x_{Ba}	ΔG_{Ba} [J/mol]	ΔH_{Ba} [J/mol]	ΔS_{Ba} [J/(mol·K)]	G^E_{Ba} [J/mol]	S^E_{Ba} [J/(mol·K)]	a_{Ba}	γ_{Ba}
0.000	−∞	−72968	∞	−72968	0.000	0.000	0.001
0.100	−78731	−54359	19.145	−54359	0.000	0.001	0.006
0.200	−56237	−39202	13.382	−39202	0.000	0.005	0.025
0.300	−39887	−27144	10.010	−27144	0.000	0.023	0.077
0.400	−27532	−17834	7.619	−17834	0.000	0.074	0.185
0.500	−18257	−10920	5.763	−10920	0.000	0.178	0.356
0.600	−11458	−6052	4.247	−6052	0.000	0.339	0.565
0.700	−6652	−2877	2.966	−2877	0.000	0.533	0.762
0.800	−3406	−1044	1.855	−1044	0.000	0.725	0.906
0.900	−1318	−202	0.876	−202	0.000	0.883	0.981
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Ba(liquid)

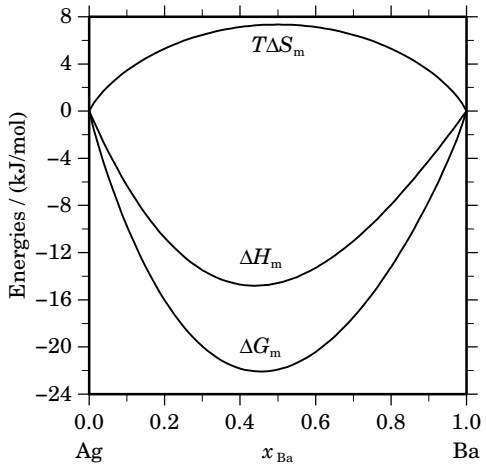

Fig. 2. Integral quantities of the liquid phase at T=1273 K.

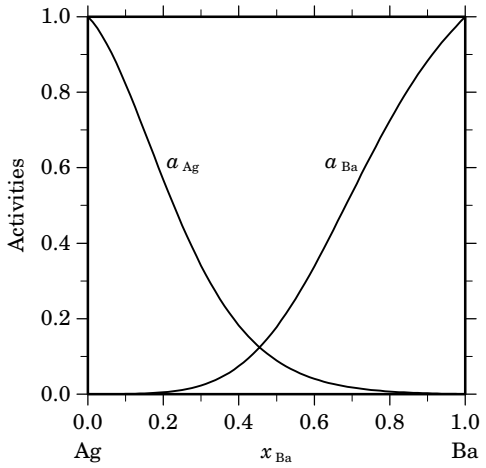

Fig. 3. Activities in the liquid phase at T=1273 K.

Table IV. Standard reaction quantities at 298.15 K for the compounds per mole of atoms.

Compound	x_{Ba}	$\Delta_{\mathrm{f}}G^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}H^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}S^{\circ}$ / (J/(mol·K))	$\Delta_{\mathrm{f}}C_P^{\circ}$ / (J/(mol·K))
Ag_5Ba_1	0.167	−11206	−11205	0.001	0.000
Ag_2Ba_1	0.333	−18356	−18356	0.001	0.000
Ag_1Ba_1	0.500	−17045	−17045	0.001	0.000
Ag_2Ba_3	0.600	−13868	−13868	0.001	0.000

References

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