Ag – Ce (Silver – Cerium)

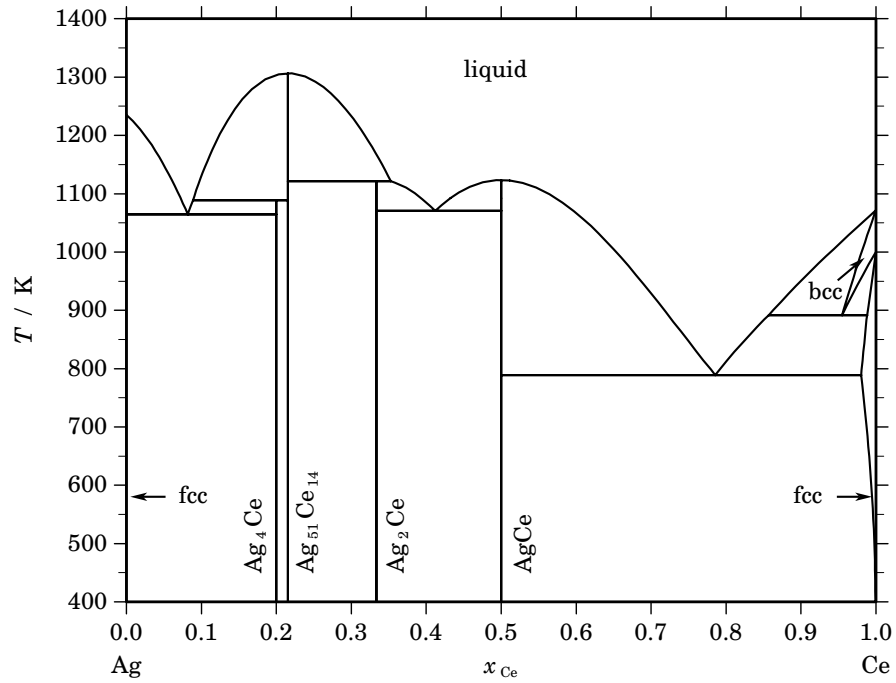

Fig. 1. Calculated phase diagram for the system Ag-Ce.

Ag-rare earth binary alloys are potential electronic materials and amorphous materials. They attract the interest of theoretical research and industrial purposes.

The phase diagram of the the Ag-Ce system has been studied in several investigations [1943Rol, 1970McM, 1975Del, 1980Heu, 1983Sta, 1984Sta] with some disagreement on the number of the intermetallic phases, their stoichiometry and the data of the invariant reactions. A review on the the literature of the Ag-Ce system has been given in [1985Gsc] and the existence of four stable intermetallic compounds has been accepted: Ag_4Ce, $Ag_{51}Ce_{14}$, Ag_2Ce and AgCe. [1980Heu] reported the maximum solubility of Ce in Ag and the solubility of Ag in Ce has been reported by [1975Del, 1983Sta]. [1987Iva] measured the thermodynamic activity of liquid phase at 1090°C by means of the Knudsen effusion method and found a large deviation from ideal behaviour. [1992Iva] determined the heats of mixing of liquid alloys of the Ag-Ce system by means of isoperibolic calorimetry. [1993Fit] measured the standard enthalpies of formation of AgCe, $Ag_{51}Ce_{14}$ and the enthalpies of mixing of the liquid, which agreed well with that of [1992Iva]. The measured standard enthalpy of formation of AgCe is abnormally less negative compared to that of equi-atomic compounds in other Ag-rare earth systems.

The thermodynamic assessment of the Ag-Ce system is from [2002Yin]. The terminal solid solutions fcc, bcc, hcp and the liquid phase were described by a substitutional solution model using the Redlich-Kister equation. The intermetallic compounds AgCe, Ag_2Ce, $Ag_{51}Ce_{14}$, and Ag_4Ce are treated as stoichiometric phases. Due to a lack of data the high and low temperature modifications of Ag_2Ce and AgCe have not been distinguished.

The calculated phase diagram is in excellent agreement with that reported by [1975Del, 1983Sta, 1984Sta]. The assessed enthalpy of formation of $Ag_{51}Ce_{14}$ agree very well with experimental results, the assessed value for AgCe is more negative. The agreement of optimised results with the experimental activities at 1090°C and with the experimental enthalpies of mixing is good.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Ag,Ce)_1$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$(Ag,Ce)_1$
Ag_4Ce	⋯	⋯	⋯	⋯	AG4CE	Ag_4Ce_1
$Ag_{51}Ce_{14}$	⋯	$Ag_{51}Gd_{14}$	$hP65$	$P6/m$	AG51CE14	$Ag_{51}Ce_{14}$
αAg_2Ce	⋯	Cu_2Ce	$oI12$	$Imma$	AG2CE	Ag_2Ce_1
βAg_2Ce	⋯	⋯	⋯	⋯	AG2CE	Ag_2Ce_1
γAg_2Ce	⋯	⋯	⋯	⋯	AG2CE	Ag_2Ce_1
αAgCe	$B2$	CsCl	$cP2$	$Pm\overline{3}m$	AGCE	Ag_1Ce_1
βAgCe	⋯	⋯	⋯	⋯	AGCE	Ag_1Ce_1
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Ag,Ce)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Ce}			$\Delta_r H$ / (J/mol)
liquid ⇌ $Ag_{51}Ce_{14}$	congruent	1306.7	0.215	0.215		−14455
liquid ⇌ AgCe	congruent	1123.3	0.500	0.500		−14644
$Ag_{51}Ce_{14}$ + liquid ⇌ Ag_2Ce	peritectic	1121.3	0.215	0.353	0.333	−10513
liquid + $Ag_{51}Ce_{14}$ ⇌ Ag_4Ce	peritectic	1089.0	0.089	0.215	0.200	−1524
liquid ⇌ Ag_2Ce + AgCe	eutectic	1070.4	0.412	0.333	0.500	−12794
liquid ⇌ fcc + Ag_4Ce	eutectic	1064.5	0.082	0.000	0.200	−10720
bcc ⇌ liquid + fcc	metatectic	891.8	0.955	0.857	0.988	−795
liquid ⇌ AgCe + fcc	eutectic	789.0	0.786	0.500	0.980	−9716

Table IIIa. Integral quantities for the liquid phase at 1323 K.

x_{Ce}	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	−10380	−8832	1.170	−6804	−1.532	0.000
0.200	−17064	−14566	1.888	−11560	−2.272	0.000
0.300	−21187	−17628	2.690	−14467	−2.389	0.000
0.400	−23131	−18444	3.543	−15728	−2.053	0.000
0.500	−23169	−17439	4.331	−15544	−1.432	0.000
0.600	−21520	−15039	4.899	−14117	−0.697	0.000
0.700	−18367	−11670	5.062	−11647	−0.017	0.000
0.800	−13842	−7756	4.600	−8337	0.439	0.000
0.900	−7963	−3724	3.204	−4388	0.501	0.000
1.000	0	0	0.000	0	0.000	0.000

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

Table IIIb. Partial quantities for Ag in the liquid phase at 1323 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	−2217	−1620	0.452	−1058	−0.424	0.817	0.908
0.800	−6419	−5912	0.383	−3964	−1.472	0.558	0.697
0.700	−12239	−12024	0.162	−8315	−2.804	0.329	0.470
0.600	−19327	−19106	0.167	−13708	−4.080	0.173	0.288
0.500	−27365	−26307	0.800	−19741	−4.963	0.083	0.166
0.400	−36089	−32774	2.506	−26009	−5.113	0.038	0.094
0.300	−45356	−37657	5.819	−32112	−4.191	0.016	0.054
0.200	−55349	−40104	11.523	−37645	−1.859	0.007	0.033
0.100	−67535	−39265	21.368	−42207	2.223	0.002	0.022
0.000	−∞	−34288	∞	−45393	8.394	0.000	0.016

Reference state: Ag(liquid)

Table IIIc. Partial quantities for Ce in the liquid phase at 1323 K.

x_{Ce}	ΔG_{Ce} [J/mol]	ΔH_{Ce} [J/mol]	ΔS_{Ce} [J/(mol·K)]	G^E_{Ce} [J/mol]	S^E_{Ce} [J/(mol·K)]	a_{Ce}	γ_{Ce}
0.000	−∞	−105226	∞	−78962	−19.852	0.000	0.001
0.100	−83850	−73741	7.641	−58521	−11.504	0.000	0.005
0.200	−59646	−49185	7.907	−41942	−5.474	0.004	0.022
0.300	−42066	−30705	8.587	−28822	−1.423	0.022	0.073
0.400	−28838	−17451	8.607	−18759	0.988	0.073	0.182
0.500	−18973	−8572	7.862	−11348	2.099	0.178	0.356
0.600	−11808	−3216	6.494	−6189	2.247	0.342	0.570
0.700	−6800	−532	4.738	−2877	1.772	0.539	0.770
0.800	−3465	331	2.869	−1010	1.014	0.730	0.912
0.900	−1344	225	1.186	−185	0.310	0.885	0.983
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Ce(liquid)

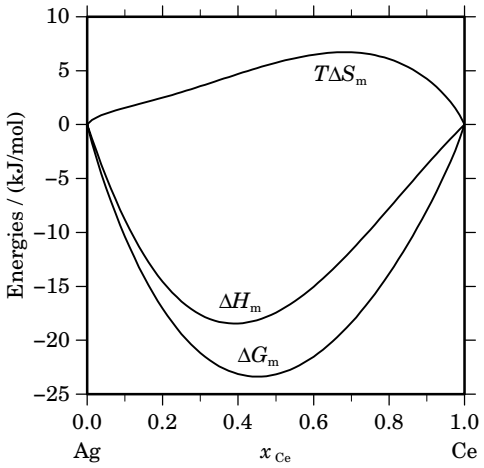

Fig. 2. Integral quantities of the liquid phase at T=1323 K.

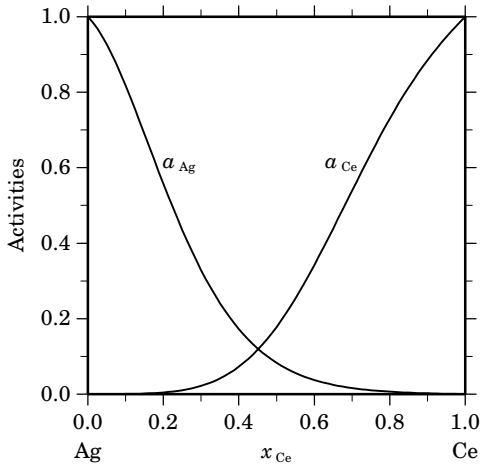

Fig. 3. Activities in the liquid phase at T=1323 K.

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

Compound	x_{Ce}	$\Delta_{\mathrm{f}}G^{\circ}$ / (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_4Ce_1	0.200	−17765	−17863	−0.329	0.000
$Ag_{51}Ce_{14}$	0.215	−18949	−18998	−0.166	0.000
Ag_2Ce_1	0.333	−20412	−20194	0.734	0.000
Ag_1Ce_1	0.500	−22272	−22331	−0.197	0.000

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