High temperature thermodynamics of Cerium Silicates, A-Ce$_2$Si$_2$O$_7$, and Ce$_{4.67}$(SiO$_4$)$_3$O

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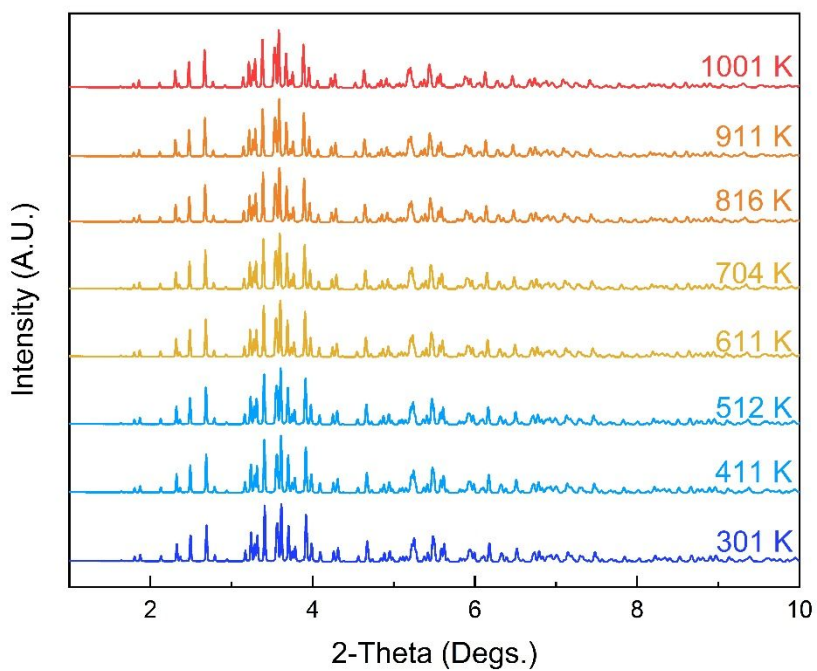
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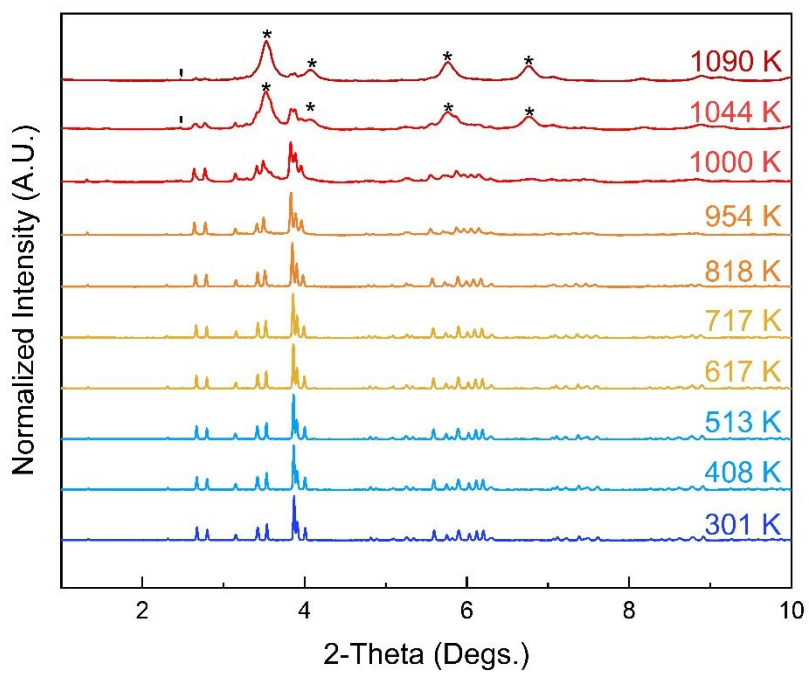**Figure S1:** Synchrotron XRD patterns of A-Ce$_2$Si$_2$O$_7$ at every ~100K intervals.

Figure S2: Synchrotron XRD patterns of Ce$_{4.67}$(SiO$_4$)$_3$O. Symbol * denotes ceria (CeO$_2$) and ' denotes beta-quartz (SiO$_2$).
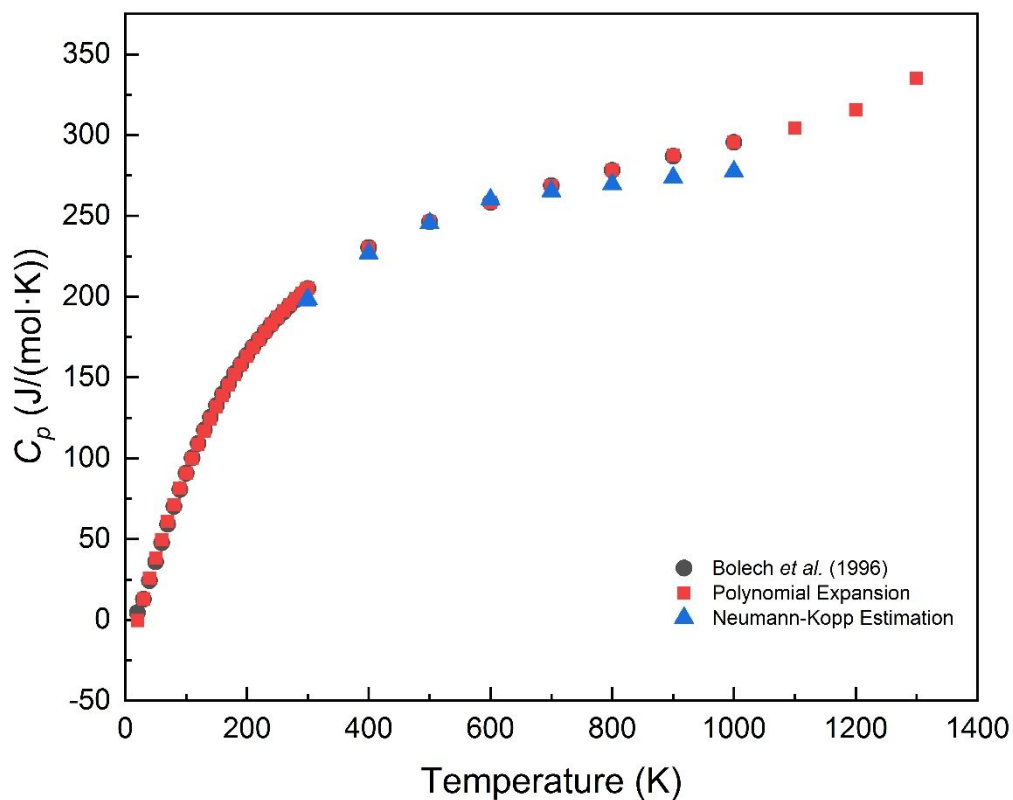
Figure S3: Comparison of three different heat capacities data for G-$Ce_2Si_2O_7$. Data is from experimental data reported in Bolech et al.[1] (*grey)*, fifth-order polynomial fitting to expand the data reported by Bolech et al.[1] from 1000 to 1300 K (*red*), and estimation of C_p through Neumann-Kopp rule (*blue*). Data of the binary oxides (CeO_2 and SiO_2) utilized for estimation using Neumann-Kopp was taken from Robie and Hemingway[2].

Table S1: Thermochemical cycles used for calculations of the enthalpy of formation from binary oxides and the standard enthalpy of formation of stetindite based on the data of drop solution calorimetry in molten lead borate at 973 K.

| Reaction	ΔH (kJ/mol)
(1) $CeSiO_4 \cdot 0.025H_2O_{(s,\ 298\ K)} \rightarrow CeO_{2(sln,\ 973\ K)} + SiO_{2(cristobalite,\ 973\ K)} + 0.025H_2O_{(g,\ 973\ K)}$	$\Delta H_1 = 137.17^*$ (1) [‡]
(2) $CeO_{2(s,\ 298\ K)} \rightarrow CeO_{2(sln,\ 973\ K)}$	$\Delta H_2 = 122.90 \pm 2.6$ [3]
(3) $SiO_{2(quartz,\ 298\ K)} \rightarrow SiO_{2(cristobalite,\ 973\ K)}$	$\Delta H_3 = 39.4 \pm 0.4$ [4]
(4) $Ce_{(s,\ 298\ K)} + O_{2(g,\ 298K)} \rightarrow CeO_{2(s,\ 298\ K)}$	$\Delta H_4 = -1088.7 \pm 1.5$ [2]
(5) $Si_{(s,\ 298\ K)} + O_{2(g,\ 298\ K)} \rightarrow SiO_{2(quartz,\ 298\ K)}$	$\Delta H_5 = -910.7 \pm 1.0$ [2]
(6) $H_2O_{(l,\ 298\ K)} \rightarrow H_2O_{(g,\ 298\ K)}$	$\Delta H_6 = 69.0$ [5]

Corrected enthalpy of drop solution value assuming H_2O behaves like liquid water, and the enthalpy of formation of stetindite from CeO_2, SiO_2 (quartz):

$\Delta H_{ds}(CeSiO_4) = \Delta H_1 - 0.025 \cdot \Delta H_6 = 133.64$ kJ/mol

$CeO_{2(s,\ 298\ K)} + SiO_{2(quartz,\ 298\ K)} \rightarrow CeSiO_{4(s,\ 298\ K)}$
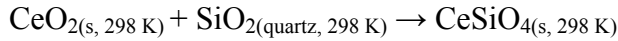
$\Delta H_{f,ox}(CeSiO_4) = -\Delta H_{ds}(CeSiO_4) + \Delta H_2 + \Delta H_3 = 28.7 \pm 2.6$ kJ/mol

Standard enthalpy of formation of stetindite:

$Ce_{(s,\ 298\ K)} + Si_{(s,\ 298\ K)} + 2O_{2(g,\ 298\ K)} \rightarrow CeSiO_{4(s,\ 298\ K)}$
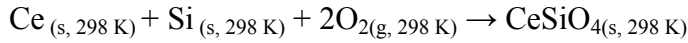
$\Delta H^{\circ}_f(CeSiO_4) = \Delta H_{f,ox}(CeSiO_4) + \Delta H_4 + \Delta H_5 = -1970.7 \pm 3.2$ kJ/mol

[*] Average. [†] Two standard deviations of the average value. [‡] Number of measurements.

Table S2: Table of thermodynamic variables needed to calculated ΔG_{rxn} at 1300 K to assess the external stability of A-$Ce_2Si_2O_7$.

(1) $Ce_2Si_2O_{7(s, \, 298 \, K)}$	$S°_1 = 186.2 \pm 5.6$ J/mol·K[c]
(2) $CeSiO_{4(s, \, 298 \, K)}$	$S°_2 = 97.4 \pm 2.9$ J/mol·K[c]
(3) $Ce_{(s, \, 298 \, K)}$	$S°_3 = 72.0 \pm 4.0$ J/mol·K[2]
(4) $Si_{(s, \, 298 \, K)}$	$S°_4 = 41.5 \pm 0.1$ J/mol·K[2]
(5) $O_{2(g, \, 298 \, K)}$	$S°_5 = 205.2 \pm 0.02$ J/mol·K[2]
(6) $Ce_2Si_2O_{7(s)}$	$\Delta C_{P \, 1300-298} = 33.3$ J/mol·K [a]
(7) $CeSiO_{4(s)}$	$\Delta C_{P \, 1300-298} = 47.2$ J/mol·K [b]
(8) $CeO_{2(s)}$	$\Delta C_{P \, 1300-298} = 19.8$ J/mol·K[2]
(9) $SiO_{2 \, (s)}$	$\Delta C_{P \, 1300-298} = 27.4$ J/mol·K[2]
(10) $H_2O_{(g)}$	$\Delta C_{P \, 1300-298} = 9.7$ J/mol·K[5]
(11) $O_{2(g)}$	$\Delta C_{P \, 1300-298} = 6.6$ J/mol·K[5]
(12) $H_{2 \, (g)}$	$\Delta C_{P \, 1300-298} = 2.0$ J/mol·K[5]
(13) $Ce_2Si_2O_{7(s, \, 298 \, K)} + ((\Delta C_P \times (1300 - 298.15))/1000)^a \rightarrow Ce_2Si_2O_{7(s, \, 1300 \, K)}$	$\Delta H_1 = -3694.3 \pm 6.0$ kJ/mol
(14) $CeSiO_{4(s, \, 298 \, K)} + ((\Delta C_P \times (1300 - 298.15))/1000)^b \rightarrow CeSiO_{4(s, \, 1300 \, K)}$	$\Delta H_2 = -1924.6 \pm 3.6$ kJ/mol[6]
(15) $CeO_{2(s, \, 298 \, K)} + ((\Delta C_P \times (1300 - 298.15))/1000) \rightarrow CeO_{2(s, \, 1300 \, K)}$	$\Delta H_3 = -1068.8 \pm 1.3$ kJ/mol[2]
(16) $SiO_{2(quartz, \, 298 \, K)} + ((\Delta C_P \times (1300 - 298.15))/1000) \rightarrow SiO_{2(cristobalite, \, 1300 \, K)}$	$\Delta H_4 = -844.4 \pm 2.1$ kJ/mol[2]
(17) $H_2O_{(g, \, 298 \, K)} + ((\Delta C_P \times (1300 - 298.15))/1000) \rightarrow H_2O_{(g, \, 1300 \, K)}$	$\Delta H_5 = -202.9 \pm 0.04$ kJ/mol[5]
(18) $O_{2(g, \, 298 \, K)} + ((\Delta C_P \times (1300 - 298.15))/1000) \rightarrow O_{2(g, \, 1300 \, K)}$	$\Delta H_6 = 33.3 \pm 0.02$ kJ/mol[5]
(19) $H_{2 \, (g, \, 298 \, K)} + ((\Delta C_P \times (1300 - 298.15))/1000) \rightarrow H_{2(g, \, 1300 \, K)}$	$\Delta H_7 = 29.9$ kJ/mol[5]
(20) $Ce_2Si_2O_{7(s, \, 298 \, K)}$	$\Delta G_1 = -3599.0 \pm 10.0$ kJ/mol[d]
(21) $CeSiO_{4(s, \, 298 \, K)}$	$\Delta G_2 = -1844.8 \pm 6.1$ kJ/mol[d]
(22) $Ce_2Si_2O_{7(s, \, 1300 \, K)}$	$\Delta G_3 = -2707.9 \pm 10.0$ kJ/mol[d]
(23) $CeSiO_{4(s, \, 1300 \, K)}$	$\Delta G_4 = -1370.2 \pm 6.1$ kJ/mol[d]
(24) $CeO_{2(s, \, 1300 \, K)}$	$\Delta G_5 = -815.2 \pm 1.9$ kJ/mol[2]
(25) $SiO_{2(cristobalite, \, 1300 \, K)}$	$\Delta G_6 = -679.7 \pm 2.1$ kJ/mol[2]
(26) $H_2O_{(g, \, 1300 \, K)}$	$\Delta G_7 = -175.7 \pm 0.1$ kJ/mol[2]
(27) $O_{2(g, \, 1300 \, K)}$	$\Delta G_8 = -117.1 \pm 0.0$ kJ/mol[2]
(28) $H_{2(g, \, 1300 \, K)}$	$\Delta G_9 = -198.5 \pm 0.0$ kJ/mol[2]

Standard Entropy of Formation of $Ce_2Si_2O_7$:

$\Delta S_f = S°(1) - (2 \times S°_2) - (2 \times S°_3) - (3.5 \times S°_4) = -758.8 \pm 8.0$ J/mol·K

Standard Entropy of Formation of $CeSiO_4$:

$\Delta S_f = S°(2) - S°_2 - S°_3) - (2 \times S°_4) = -426.4 \pm 5.0$ J/mol·K

Reaction (1): A-$Ce_2Si_2O_7$ reacting with oxygen at 1300 K and forming $CeSiO_4$

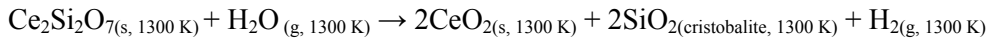$Ce_2Si_2O_{7(s, 1300 K)} + 0.5O_{2(g, 1300 K)} \rightarrow 2CeSiO_{4(s, 1300 K)}$
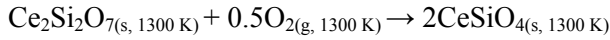
$\Delta G_{rxn} = 2\Delta G_4 - \Delta G_3 - 0.5\Delta G_8 = 66.7 \pm 13.2$ kJ/mol

Reaction (2): A-$Ce_2Si_2O_7$ reacting with oxygen at 1300 K and forming CeO_2 and SiO_2

$Ce_2Si_2O_{7(s, 1300 K)} + 0.5O_{2(g, 1300 K)} \rightarrow 2CeO_{2(s, 1300 K)} + 2SiO_{2(cristobalite, 1300 K)}$
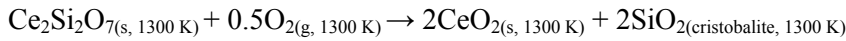
$\Delta G_{rxn} = 2\Delta G_5 + 2\Delta G_6 - \Delta G_3 - 0.5\Delta G_8 = -182.7 \pm 10.7$ kJ/mol

Reaction (3): A-$Ce_2Si_2O_7$ reacting with steam at 1300 K and forming $CeSiO_4$ and H_2

$Ce_2Si_2O_{7(s, 1300 K)} + H_2O_{(g, 1300 K)} \rightarrow 2CeSiO_{4(s, 1300 K)} + H_{2(g, 1300 K)}$
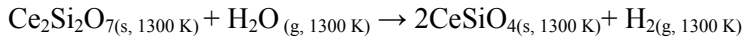
$\Delta G_{rxn} = 2\Delta G_4 + \Delta G_9 - \Delta G_3 - \Delta G_7 = 26.1 \pm 13.2$ kJ/mol

Reaction (4): A-$Ce_2Si_2O_7$ reacting with steam at 1300 K and forming CeO_2, SiO_2, and H_2

$Ce_2Si_2O_{7(s, 1300 K)} + H_2O_{(g, 1300 K)} \rightarrow 2CeO_{2(s, 1300 K)} + 2SiO_{2(cristobalite, 1300 K)} + H_{2(g, 1300 K)}$

$\Delta G_{rxn} = 2\Delta G_5 + 2\Delta G_6 + \Delta G_9 - \Delta G_3 - \Delta G_7 = -223.3 \pm 10.7$ kJ/mol

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[a] Expanded heat capacity equation of Bolech *et al.* (1996)[1]; [b] Heat capacity derived through NKR of CeO_2[2] and SiO_2[2]; [c] $S°$ estimated through use of the empirical relationship developed for silicate minerals by Jenkins and Glasser (2003)[7]; [d] $\Delta G_T = \Delta H_T - TS$

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