

Metastability of Spinel-type Solid Solutions in the $\text{SiO}_2\text{--Al}_2\text{O}_3$ System

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The addition of small amounts (2–10 wt %) of SiO_2 to $\gamma\text{-Al}_2\text{O}_3$ increases the temperature of heat treatment necessary for transformation to $\alpha\text{-Al}_2\text{O}_3$ by ~ 100 K. We have studied this system using high-temperature solution calorimetry in molten $2\text{PbO}\cdot\text{B}_2\text{O}_3$ at 1043 K. Our results indicate that the spinel-type $\text{Al}_2\text{O}_3\text{--SiO}_2$ solid solutions with 2–10 wt % SiO_2 are always energetically metastable by 30–35 $\text{kJ}\cdot\text{mol}^{-1}$ (on a 4 O^{2-} per mole basis) with respect to $\alpha\text{-Al}_2\text{O}_3$ and quartz. Calculation of the maximum configurational entropy of the solid solutions allowed determination of the likely most negative value of the Gibbs free energy of the materials. The solid solutions are somewhat entropy stabilized, but still thermodynamically metastable by > 10 $\text{kJ}\cdot\text{mol}^{-1}$ at 1400 K. Therefore, SiO_2 addition appears to provide mainly a kinetic hindrance to $\alpha\text{-Al}_2\text{O}_3$ formation.

Introduction

Transition aluminas are widely used as high surface area supports for noble metal (i.e., Pt, Pd, Rh) hydrocarbon combustion catalysts.¹ Under operating conditions (e.g., in automotive exhaust treatment), these catalysts are often subjected to H_2O vapor at temperatures in excess of 1273 K. These conditions have been shown to reduce drastically the specific surface area of $\gamma\text{-Al}_2\text{O}_3$, which effectively reduces the activity of the catalysts and shortens their usable lifetimes. Small additions of about 2–10 wt % of SiO_2 to Al_2O_3 stabilize $\gamma\text{-Al}_2\text{O}_3$ against loss of specific surface area when the material is exposed to H_2O vapor at elevated temperatures.² SiO_2 addition increases the temperature necessary for complete transformation to $\alpha\text{-Al}_2\text{O}_3$ by about 100 K.^{2,3} These factors make $\text{SiO}_2\text{--Al}_2\text{O}_3$ solid solutions promising candidates for high surface area catalytic supports under harsh conditions.

The formation of an aluminosilicate spinel with an X-ray diffraction pattern similar to $\gamma\text{-Al}_2\text{O}_3$ has been frequently observed upon calcination of sol–gel precursors to mullite. The exact composition of this phase has been the subject of some debate. Chakravorty et al.⁴ believed the phase to be a cubic modification of mullite, with identical $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ stoichiometry. Brown et al.⁵ have reported NMR evidence which suggested that the spinel phase was much closer in composition to pure $\gamma\text{-Al}_2\text{O}_3$ than to mullite. Sonuparlak et al.⁶ and Okada

and Otsuka⁷ proposed that the spinel phase was a solid solution of ~ 8 wt % SiO_2 in Al_2O_3 with a $\gamma\text{-Al}_2\text{O}_3$ structure, which might be thermodynamically stable with respect to $\alpha\text{-Al}_2\text{O}_3$ and SiO_2 . This ~ 8 wt % SiO_2 in Al_2O_3 composition was supported by an analytical transmission electron microscopy (TEM) study of NaOH treated samples.⁶ Gerardin et al.⁸ later reported the SiO_2 content to be ~ 7 wt % based on ^{29}Si NMR. In this contribution, we present an assessment of the thermodynamic stability of these aluminosilicate spinel solid solutions with 0–10 wt % SiO_2 . The materials were studied using high-temperature solution calorimetry in molten $2\text{PbO}\cdot\text{B}_2\text{O}_3$ at 1043 K. In addition, the maximum configurational entropy contribution to the free energy of each solid solution was calculated. Our results indicate that $\text{Al}_2\text{O}_3\text{--SiO}_2$ solid solutions are always metastable with respect to $\alpha\text{-Al}_2\text{O}_3$ and quartz and suggest that the apparent stabilization achieved upon SiO_2 addition has kinetic origins.

Experimental Procedure

Sample Preparation. Aluminosilicate solid solutions were prepared with 0, 2, 4, 6, 8, 10, 12, and 16 wt % SiO_2 . Samples were synthesized by spray drying. Approximately 0.10 mol $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ was dissolved in 100 mL of 95% ethanol. The appropriate amount of $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ (tetraethoxysilane, TEOS) for the desired silica content was added. The resulting solution was stirred for 1.5 h to ensure homogeneity and then sprayed onto a heated aluminum pan. The temperature of the pan was adjusted to maximize the rate of drying and minimize spattering of the solution from the surface. The resulting precursors were then denitrated by calcination at 773 K. Phase formation was studied by calcining the denitrated precursor at various temperatures between 1073 and 1773 K. Calorimetry was performed on samples calcined at 1273 K for 6 h. $\gamma\text{-Al}_2\text{O}_3$ (0 wt % SiO_2) and $\alpha\text{-Al}_2\text{O}_3$ were prepared by an

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analogous procedure from a precursor without TEOS addition via calcination at 1203 and 1773 K, respectively.

Sample Characterization. The precursor decomposition and product formation were studied by simultaneous thermogravimetric and differential thermal analysis (TGA/DTA) (Rheometrics Model STA 1500H, Piscataway, NJ) and powder X-ray diffraction (XRD) (Philips Electronics, APD 3270, Mahwah, NJ). Three separate TGA/DTA experiments were performed for each SiO₂ content: (1) on the "as-prepared" precursor, (2) on the precursor after denitration at 773 K, and (3) on the sample for calorimetry after calcination at 1273 K and equilibration of the adsorbed H₂O content with the atmosphere of the calorimetry laboratory (see below). The first two TGA/DTA experiments were performed at 10 K·min⁻¹ to 1273 K and held for 1 h at 1273 K before cooling to room temperature. The third TGA experiment was performed at 10 K·min⁻¹ to 1043 K, held for 1 h at 1043 K, and then heated at 10 K·min⁻¹ to 1773 K. This procedure allowed determination of the total adsorbed H₂O content and the H₂O content that remained adsorbed after transposed temperature drop calorimetry (see below).

Calorimetry. High-temperature drop solution calorimetry was performed in a Tian-Calvet twin calorimeter, described in detail by Navrotsky,⁹ operating at ~1043 K with 2PbO·B₂O₃ as the solvent. Samples were pressed into pellets of ~10–20 mg and dropped, from room temperature, into molten 2PbO·B₂O₃ located in the hot zone of the calorimeter. The measured heat effect was a combination of the heat content and heat of solution of the sample. Heat effects were calibrated against the heat content of Pt by dropping ~200 mg pieces of Pt wire from room temperature into the calorimeter. Due to their relatively high specific surface area, the spinel-type aluminosilicate solid solutions adsorbed significant amounts of atmospheric water, the removal of which also contributed to the measured heat effects. To ensure a stable, equilibrium H₂O content, as in previous studies on nanophase aluminas¹⁰ and AlPO₄ zeolites,¹¹ the samples were exposed to the air in the calorimetry laboratory, which has a precisely controlled environment (295 ± 1 K and 55 ± 2% relative humidity), for ≥ 7 days. The equilibrium water content on each sample was then determined thermogravimetrically as described above. All calorimetric experiments were run under flowing Ar (90 mL/min) to flush evolved H₂O from the calorimeter. It has been previously demonstrated that under these conditions the water does not remain in or interact energetically with the solvent, and exits the calorimeter as vapor.¹²

To evaluate the heat effect due to removal of H₂O from the samples, transposed temperature drop calorimetry, wherein the sample was dropped into empty (without solvent) platinum crucibles, was performed in the same calorimeter. The measured heat effect from transposed temperature drop experiments was the heat content of the sample and the heat due to water removal. However, all of the adsorbed H₂O on these samples was not desorbed during the transposed temperature drop experiments, which heated the sample to 1043 K (the calorimeter temperature) for ~1 h. Therefore, the weight percentage of H₂O remaining on the samples after a 1 h heat treatment under flowing Ar was determined for each sample via TGA as described above. This tightly bound H₂O, which usually amounted to ~0.3 wt %, is removed during drop solution calorimetry, as the sample completely dissolves in the lead borate solvent. Removal of this strongly chemisorbed H₂O contributes to the measured enthalpy of drop solution calorimetry. Therefore, the data from transposed temperature drop experiments must be corrected to determine the enthalpy of solution of the aluminosilicate solid solutions (see below). Coster et al.¹³ and Gervasini and Auroux¹⁴ have shown that the initial heat of adsorption of H₂O onto transition aluminas

Table 1. Summary of XRD Results on Aluminosilicate Samples^a

calcination temp (K)	0% SiO ₂	2% SiO ₂	4% SiO ₂	6% SiO ₂	8% SiO ₂	10% SiO ₂
1073	γ-Al ₂ O ₃	amorph	amorph	amorph	amorph	amorph
1273	α-Al ₂ O ₃	γ-Al ₂ O ₃	γ-Al ₂ O ₃	γ-Al ₂ O ₃	γ-Al ₂ O ₃	γ-Al ₂ O ₃
1373	α-Al ₂ O ₃	γ-Al ₂ O ₃	γ-Al ₂ O ₃	γ-Al ₂ O ₃	γ-Al ₂ O ₃	γ-Al ₂ O ₃
1473	α-Al ₂ O ₃	γ-Al ₂ O ₃	γ-Al ₂ O ₃	γ-Al ₂ O ₃	γ-Al ₂ O ₃	γ-Al ₂ O ₃
1573	α-Al ₂ O ₃	α-Al ₂ O ₃	α-Al ₂ O ₃	α-Al ₂ O ₃	α-Al ₂ O ₃	α-Al ₂ O ₃

^a Amorph signifies no crystalline phases were detected. γ-Al₂O₃ denotes material with an XRD pattern similar to that of gamma alumina. α-Al₂O₃ signifies material where some α-Al₂O₃ was detected.

can exceed 200 kJ·mol⁻¹ H₂O. Coster et al.¹³ fitted their adsorption data to Freundlich curves, which when integrated yield an average of 132.9 kJ·mol⁻¹ for the integral heat of chemisorption of H₂O for coverages of 5.4 OH/nm². As our samples are ≥ 90 wt % Al₂O₃, this value should also be acceptable for the aluminosilicates, but as the final state of transposed temperature drop calorimetry is H₂O vapor at 979 K, the heat content of H₂O between 298 and 1043 K, 28.5 kJ·mol⁻¹, needs to be added to the heat of adsorption. The transposed temperature drop calorimetry data were then corrected for the H₂O remaining adsorbed at 1043 K by adding 160 ± 10 kJ·mol⁻¹ H₂O to the measured value.

Results

The thermal decomposition of the precursor (as prepared) was studied by simultaneous TGA/DTA. A broad endotherm was observed at ~523 K, and two discrete exotherms were observed at ~623 and ~1173 K. The 523 K endotherm can be attributed to nitrate decomposition, while the 623 K exotherm might have been due to oxidation of residual organic material. The results of XRD experiments are summarized in Table 1. Powder XRD patterns of products obtained from calcination of precursors with 2–10 wt % SiO₂ at 1073 K were devoid of Bragg scattering, while calcination of the 0% SiO₂ sample at 1073 K yielded an XRD pattern which could be indexed to γ-Al₂O₃. Calcination of precursors with 2–10 wt % SiO₂ at 1273 K yielded aluminosilicate material with an XRD pattern similar to that of γ-Al₂O₃. This indicates that the DTA exotherm observed at ~1173 K is due to crystallization of this spinel-type structure from the amorphous material. Mullite was detected by XRD after calcination of the 16 wt % SiO₂ sample at 1273 K. The exact temperature of crystallization of the spinel-type solid solution (or mullite), as judged by the temperature at which the second exotherm was observed via DTA, increased linearly with increasing SiO₂ content up to about 10% (see Figure 1). In all SiO₂-doped samples, the minimum calcination temperature necessary for formation of α-Al₂O₃ was greater than 1473 K. Calcination of the pure Al₂O₃ precursor (0% SiO₂) at only 1273 K resulted in partial transformation to α-Al₂O₃ (detected via XRD), thus demonstrating the expected suppression of α-Al₂O₃ formation in the SiO₂-doped samples.

To determine if the apparent stabilization of the aluminosilicate spinel-type solid solution with respect to transformation to α-Al₂O₃ has an energetic origin, high-temperature solution calorimetry was performed on samples with 0–10 wt % SiO₂ calcined at 1273 K.

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Table 2. Results of Sample Characterization and Calorimetry^a

SiO ₂ content (wt %)	calcination temp (K)	x in Al _{8/3-4/3x} Si _x O ₄	% H ₂ O		ΔH_{ds} (J/g) ^b	ΔH_{ttd} (J/g) ^c	ΔH_{cttd} (J/g) ^d	ΔH_{soln} (J/g) ^e	ΔH_{soln} (kJ·mol ⁻¹) ^e
			298 K	1043 K					
0 (α)	1773	0	0.00	0.00	1093.8 ± 14.1 (5)	775.9 ± 9.7 (6)	775.9 ± 9.7	318.0 ± 17.2	43.2 ± 2.3
0 (γ)	1213	0	4.81	0.39	1059.9 ± 12.7 (6)	988.4 ± 9.2 (6)	1023.1 ± 9.5	38.6 ± 16.7	5.3 ± 2.3
2	1273	0.0451	2.66	0.29	978.7 ± 9.9 (6)	894.8 ± 7.2 (6)	920.5 ± 7.3	59.7 ± 12.7	8.1 ± 1.7
4	1273	0.0900	3.04	0.29	1003.8 ± 3.5 (6)	906.8 ± 14.4 (6)	932.6 ± 14.5	73.4 ± 15.3	9.9 ± 2.1
6	1273	0.1347	2.32	0.29	947.9 ± 4.2 (6)	863.0 ± 14.6 (6)	888.8 ± 14.6	60.5 ± 15.6	8.2 ± 2.1
8	1273	0.1791	2.04	0.28	932.4 ± 16.0 (6)	857.8 ± 5.1 (6)	882.6 ± 5.3	50.8 ± 17.2	6.8 ± 2.3
10	1273	0.2233	0.88	0.25	882.7 ± 8.7 (6)	799.4 ± 12.3 (6)	821.6 ± 12.4	61.6 ± 15.3	8.3 ± 2.0

^a Reported uncertainties are two standard deviations of the mean. Number in parentheses is the number of experiments performed.

^b Measured enthalpy of drop solution calorimetry. ^c Measured enthalpy of transposed temperature drop calorimetry. ^d Enthalpy of transposed temperature drop calorimetry corrected for H₂O remaining adsorbed at 1043 K. ^e Calculated enthalpy of solution of Al_{8/3-2x}Si_{2x}O_{4+x} in 2PbO·B₂O₃ at 1043 K.

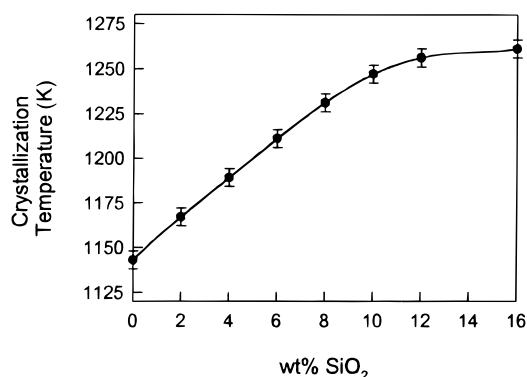
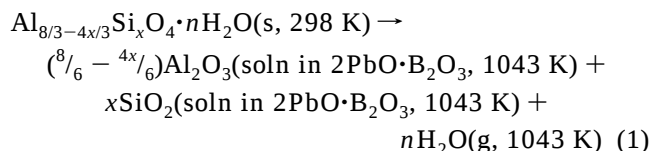
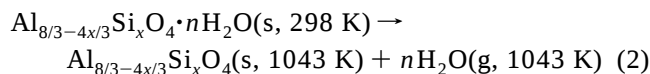


Figure 1. Temperature of crystallization of a spinel-type aluminosilicate solid solution from amorphous aluminosilicate precursors as a function of SiO₂ content. Crystallization temperatures determined via DTA. The temperature reported for the 16 wt % SiO₂ sample corresponds to mullite formation

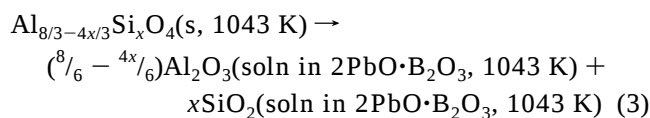
To eliminate heat effects due to adsorbed H₂O, two separate calorimetric experiments were performed on each sample. In the first experiment, drop solution calorimetry, the sample (with equilibrium adsorbed H₂O content) is dropped into molten 2PbO·B₂O₃ in the calorimeter. The measured heat effect, ΔH_{ds} , is that accompanying the reaction:



In the second experiment, transposed temperature drop calorimetry, the sample is dropped into empty (without solvent) Pt crucibles in the calorimeter. The measured heat effect, ΔH_{ttd} , is that accompanying the reaction:



By taking the difference between these two heat effects, the contribution of H₂O to the measured enthalpy can be eliminated, and the enthalpy of solution of the aluminosilicate solid solution in 2PbO·B₂O₃ at 1043 K, ΔH_{soln}



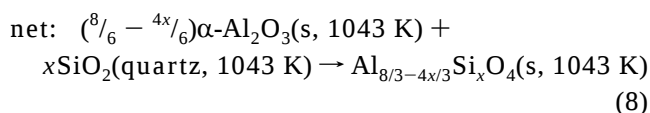
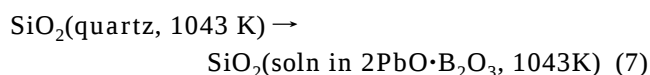
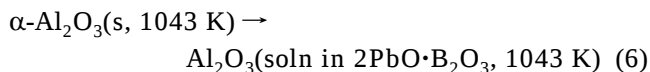
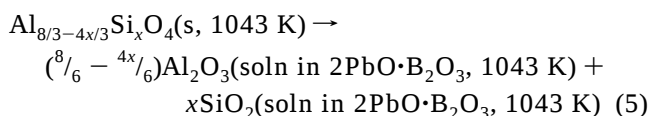
can be calculated as

$$\Delta H_{soln} = \Delta H_{ds} - \Delta H_{ttd} \quad (4)$$

However, this equation is slightly oversimplified. TGA revealed that all of the adsorbed H₂O was not removed from the samples during a 1 h heat treatment at 1043 K (i.e., during transposed temperature drop calorimetry). Therefore, the measured ΔH_{ttd} values were corrected for the remaining H₂O using a value of 160 kJ·mol⁻¹ H₂O from the recent heat of adsorption data of Coster et al.¹³ This correction generally amounted to an increase of about 3% over the measured value (see Table 2).

Discussion

The ΔH_{soln} values for the aluminosilicate solid solutions are shown in Table 2 and in Figure 2 as a function of x in the general formula Al_{8/3-4x/3}Si_xO₄. The enthalpies of solution become slightly more endothermic with initial SiO₂ addition and then decrease after about 4 wt % SiO₂. The energetic stability of the aluminosilicate solid solutions at 1043 K can be evaluated by comparing the ΔH_{soln} values to those obtained from mechanical mixtures of α-Al₂O₃ and quartz (i.e., the thermodynamically stable end members, dotted lines in Figure 2). This is illustrated through the following thermochemical cycle:



$$\Delta H_{f(1043 \text{ K})} = \Delta H_8 = -\Delta H_5 + \left(\frac{8}{6} - \frac{4x}{6}\right)\Delta H_6 + x\Delta H_7 \quad (9)$$

In the cycle above, and the discussion that follows, the solid solutions will be considered on a 4 mol O²⁻ basis in accord with the normal spinel stoichiometry. This treatment also simplifies configurational entropy calculations (see below). The enthalpy of solution of quartz

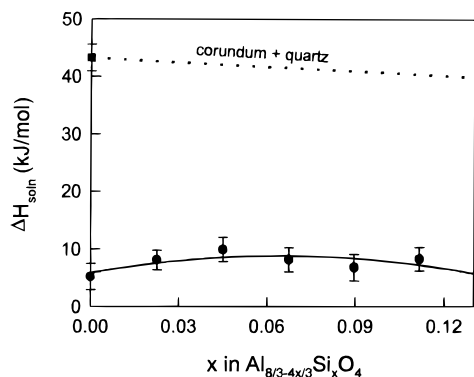


Figure 2. Enthalpies of solution of the aluminosilicate solid solutions in $2\text{PbO} \cdot \text{B}_2\text{O}_3$ at 1043 K as a function of SiO_2 content. Dotted line represents the values expected from a mechanical mixture of coarse $\alpha\text{-Al}_2\text{O}_3$ and quartz.

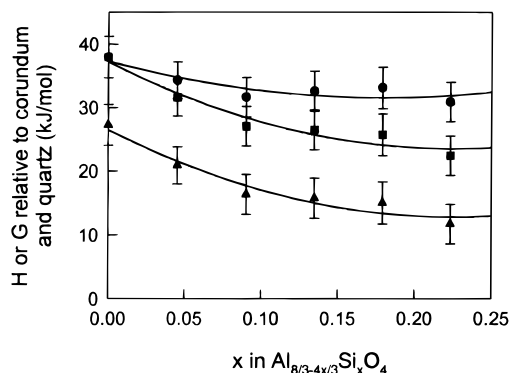


Figure 3. Enthalpies at 1043 K (●) or free energies at 1400 K of formation of the aluminosilicate solid solutions relative to a mechanical mixture of coarse $\alpha\text{-Al}_2\text{O}_3$ and quartz as a function of SiO_2 content. (■) Free energy at 1400 K including only the configurational entropy of the solid solution. (▲) Free energy at 1400 K including the configurational entropy of the solid solution and the entropy of the $\alpha\text{-Al}_2\text{O}_3 \rightarrow \gamma\text{-Al}_2\text{O}_3$ transition.

Table 3. Results of Configurational Entropy and Free Energy Calculations^a

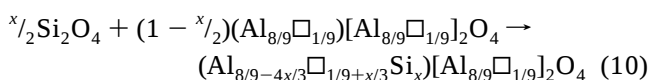
SiO ₂ content (wt %)	x in $\text{Al}_{8/3-4x/3}\text{Si}_x\text{O}_4$	H relative to $\alpha\text{-Al}_2\text{O}_3$ and SiO_2 (kJ·mol ⁻¹) ^b	G relative to $\alpha\text{-Al}_2\text{O}_3$	
			S_{config} , 1400 K (kJ·mol ⁻¹) ^c	$S_{\text{config}} + S_{\alpha \rightarrow \gamma}$, 1400 K (kJ·mol ⁻¹) ^d
0 (γ)	0	38.0 ± 3.2	38.0 ± 3.2	27.3 ± 3.2
2	0.0451	32.9 ± 2.9	31.6 ± 2.9	20.9 ± 2.9
4	0.0900	28.8 ± 3.1	27.1 ± 3.1	16.4 ± 3.1
6	0.1347	28.3 ± 3.1	26.5 ± 3.1	15.8 ± 3.1
8	0.1791	27.4 ± 3.3	25.8 ± 3.3	15.1 ± 3.3
10	0.2233	23.7 ± 3.1	22.5 ± 3.1	11.8 ± 3.1

^a Uncertainties propagated as the square root of the sum of the squares of individual uncertainties. ^b Enthalpy relative to a mechanical mixture of $\alpha\text{-Al}_2\text{O}_3$ and SiO_2 (quartz). ^c Free energy relative to $\alpha\text{-Al}_2\text{O}_3$ and SiO_2 (quartz) considering only configurational entropy contributions. ^d Free energy relative to $\alpha\text{-Al}_2\text{O}_3$ and SiO_2 (quartz) considering configurational entropy contributions and the ΔS of the $\alpha\text{-Al}_2\text{O}_3$ to $\gamma\text{-Al}_2\text{O}_3$ transition.

in $2\text{PbO} \cdot \text{B}_2\text{O}_3$, $-3.51 \pm 0.18 \text{ kJ} \cdot \text{mol}^{-1} \text{ SiO}_2$, was measured previously in our laboratory.^{15,16} The enthalpies of the aluminosilicate solid solutions relative to corundum and quartz are shown as a function of SiO_2 content are shown as the filled circles in Figure 3. Although there is a slight energetic stabilization on SiO_2 addition

to the spinel-type alumina, the solid solutions are still $>30 \text{ kJ} \cdot \text{mol}^{-1}$ less energetically stable than a mechanical mixture of $\alpha\text{-Al}_2\text{O}_3$ and quartz (see Table 3 for exact values). The slight energetic stabilization of the solid solutions (with respect to $\gamma\text{-Al}_2\text{O}_3$ and quartz) appears to plateau at about 4 wt % SiO_2 .

Due to the presence of tetrahedral and octahedral sites in the spinel structure and the fairly random distribution of Al^{3+} and vacancies over these sites, there is the potential for a large configurational entropy contribution to the free energy of the aluminosilicate solid solutions. To determine the true thermodynamic stability of the solid solutions, we calculated the maximum configurational entropy arising from SiO_2 addition and disorder of Si^{4+} , Al^{3+} , and vacancies over the available crystallographic sites. Assuming an initially random distribution of Al^{3+} ions, and inserting Si^{4+} onto only tetrahedral sites, the configurational entropy can be represented by that accompanying the reaction



where $\square$ denote vacancies, parentheses denote tetrahedral site, and square brackets denote octahedral sites. The maximum configurational entropy of the solid solution, S_{config} , is then

$$S_{\text{config}} = -R[(8/9 - 4x/3) \ln(8/9 - 4x/3) + (1/9 + x/3) \ln(1/9 + x/3) + x \ln x] - 2R[8/9 \ln(8/9) + 1/9 \ln(1/9)] \quad (11)$$

The entropy change of (10), ΔS_{config} , is then given by

$$\Delta S_{\text{config}} = S_{\text{config}}(\text{solid solution}) - (1 - x/2)S_{\text{config}}(\gamma\text{-Al}_{8/3}\text{O}_4) - x/2 S_{\text{config}}(\text{Si}_2\text{O}_4) \quad (12)$$

The configurational entropy of quartz, $S_{\text{config}}(\text{Si}_2\text{O}_4)$, is assumed to be zero. The configurational entropy of γ alumina, $S_{\text{config}}(\gamma\text{-Al}_{8/3}\text{O}_4)$, was calculated assuming a completely random distribution of Al^{3+} and vacancies over the available sites and equations similar to (10) and (11). Configurational entropy calculations for $\gamma\text{-Al}_{8/3}\text{O}_4$ are fully presented and discussed elsewhere.¹⁷ The resulting values of the configurational entropy of formation of the solid solutions are shown in Figure 4.

There is a second contribution to the entropy difference between the solid solutions and $\alpha\text{-Al}_2\text{O}_3$, the entropy of the $\alpha\text{-Al}_2\text{O}_3 \rightarrow \gamma\text{-Al}_2\text{O}_3$ transition. This entropy is also mainly configurational in nature and can be calculated similar to eqs 10 and 11 above. However, a more accurate determination can be made from data in the literature. $\gamma\text{-Al}_2\text{O}_3$ has a greater entropy than $\alpha\text{-Al}_2\text{O}_3$. At high temperatures, entropy contributions to the free energy will become dominant, and a transition from $\alpha\text{-Al}_2\text{O}_3 \rightarrow \gamma\text{-Al}_2\text{O}_3$ can be expected at a high enough temperature. No such transition has been detected up to the melting point of $\alpha\text{-Al}_2\text{O}_3$, 2327 K,¹⁸

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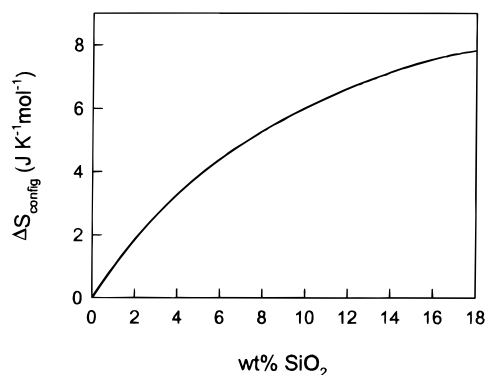


Figure 4. Calculated (using eqs 10–12) entropies of formation of the aluminosilicate solid solutions relative to a mechanical mixture of α - Al_2O_3 and quartz as a function of SiO_2 content.

but the liquid structure of alumina has been shown to have γ - Al_2O_3 character (i.e. tetrahedrally coordinated Al^{3+}).¹⁹ The lowest temperature at which the α - $\text{Al}_2\text{O}_3 \rightarrow \gamma$ - Al_2O_3 transition could occur would then be the melting point, so ΔG of the α - $\text{Al}_2\text{O}_3 \rightarrow \gamma$ - Al_2O_3 transition is equal to or greater than zero at 2327 K, and ΔS is

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equal to or greater than $5.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ Al_2O_3 or $7.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ $\text{Al}_{8/3}\text{O}_4$.

The resulting calculated values of the Gibbs free energy of the aluminosilicate solid solutions at 1400 K are given in Table 3 and graphically presented in Figure 3. With respect to corundum and quartz, the solid solutions are all thermodynamically metastable by $>10 \text{ kJ}\cdot\text{mol}^{-1}$. Thus, the apparent stability of the aluminosilicate solid solutions with respect to α - Al_2O_3 does not have a thermodynamic basis and must be a kinetic phenomenon. Our results do not explain the suppression of crystallization observed upon increasing SiO_2 content (Figure 1). This too may be a kinetic phenomenon. The transformation of amorphous alumina to γ -alumina requires rearrangement of silicon and aluminum ions and apparently the presence of silicon in solid solution poses a kinetic barrier for this transformation. We speculate that this may relate to a high energy barrier for silicon to occupy octahedral sites in the spinel structure.

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