

# Thermodynamic Description of SrO-Al<sub>2</sub>O<sub>3</sub> System and Comparison with Similar Systems

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The Al<sub>2</sub>O<sub>3</sub>-SrO binary system has been studied using the CALPHAD technique in this paper. The modeling of Al<sub>2</sub>O<sub>3</sub> in the liquid phase is modified from the traditional formula with the liquid phase represented by the ionic two-sublattice model as (Al<sup>3+</sup>, Sr<sup>2+</sup>)<sub>P</sub>(AlO<sub>2</sub><sup>1-</sup>, O<sup>2-</sup>)<sub>Q</sub>. Based on the measured phase equilibrium data and experimental thermodynamic properties, a set of thermodynamic functions has been optimized using an interactive computer-assisted analysis. The calculated results are compared with experimental data. A comparison between this system and similar systems is also given.

**Keywords** phase diagram, SrO-Al<sub>2</sub>O<sub>3</sub>, thermodynamic properties

## 1. Introduction

The SrO-Al<sub>2</sub>O<sub>3</sub> system is of interest because of the use of the intermediate compounds for hydraulic cements, laser matrices, and long-duration photoluminescence or thermoluminescence pigments.<sup>[1]</sup> But comparing with the magnesium and calcium counterparts, the knowledge of phase diagram of strontium aluminates is quite limited. Fortunately, with the help of the powerful CALPHAD technique, it is possible to obtain consistent thermodynamic description of such system from dispersed and scarce experimental information, to guide the synthesis of proper compounds to satisfy the practical requirements. Inspired by the work of re-evaluation of the liquid phases in the CaO-Al<sub>2</sub>O<sub>3</sub> and MgO-Al<sub>2</sub>O<sub>3</sub> systems by Mao et al.,<sup>[2]</sup> we have already thermodynamically assessed the BaO-Al<sub>2</sub>O<sub>3</sub> system.<sup>[3]</sup> The aim of the present work is to review the experimental studies of another one of alkali earth aluminates, i.e., SrO-Al<sub>2</sub>O<sub>3</sub> system in order to provide a consistent thermodynamic description for the system with the new liquid model proposed by Mao et al.<sup>[2]</sup> and to compare the thermodynamic properties with correlative systems.

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## 2. Experimental Information

### 2.1 Phase Diagram and Intermediate Compounds

By comparison with the closely related and better-known system CaO-Al<sub>2</sub>O<sub>3</sub>, the SrO-Al<sub>2</sub>O<sub>3</sub> phase diagram has many uncertainties, even the melting points and, more importantly, the existence of some compounds. In the system, four intermediate compounds, i.e., SrO · 6Al<sub>2</sub>O<sub>3</sub>, SrO · 2Al<sub>2</sub>O<sub>3</sub>, SrO · Al<sub>2</sub>O<sub>3</sub>, and 3SrO · Al<sub>2</sub>O<sub>3</sub> have been proven to exist for a long time.<sup>[4-8]</sup> Then, Dear<sup>[9]</sup> reported the presence of a new compound with formula 5SrO · Al<sub>2</sub>O<sub>3</sub>. However, the formula was modified to be 4SrO · Al<sub>2</sub>O<sub>3</sub> by Massazza<sup>[10,11]</sup> in 1959, who confirmed two crystalline phases for the compound at the same time, which also was confirmed thereafter by the measurement of Brisi and Abbattista.<sup>[12]</sup> A partial phase diagram including five intermediate compounds was proposed by Massazza<sup>[10,11]</sup> and is still the most frequently cited diagram. In 1973, Appendino<sup>[13]</sup> observed that long-time annealing at 1400 °C (> 200 h) resulted in partial decomposition of SrO · 2Al<sub>2</sub>O<sub>3</sub> after initially forming from the melt and considered the dialuminate to be metastable. The only complete phase diagram of this system was reported by Ganits et al.<sup>[14]</sup> in 1979; however, it was always omitted by other researchers. The compounds and phase relations are essentially the same as shown as Massazza,<sup>[10,11]</sup> except for the differences in the various melting and inversion temperatures; the dashed lines in the previous phase diagram were confirmed by experimental data. Song et al.<sup>[15]</sup> studied the sequence of phase transformation of SrO · Al<sub>2</sub>O<sub>3</sub> and 3SrO · Al<sub>2</sub>O<sub>3</sub> and observed two compounds at 1000 °C, but only SrO · Al<sub>2</sub>O<sub>3</sub> existing at 1250 °C, the latter is discrepant with other reports. The metastable compound 4SrO · 7Al<sub>2</sub>O<sub>3</sub> was synthesized by several authors,<sup>[16-19]</sup> but was not shown in any of the earlier phase diagrams.<sup>[10,11,14]</sup> André et al.<sup>[20]</sup> investigated the phase transformation concerning the 4SrO · 7Al<sub>2</sub>O<sub>3</sub> and SrO · 2Al<sub>2</sub>O<sub>3</sub>, and proposed modification of a small part of the SrO-Al<sub>2</sub>O<sub>3</sub> phase diagram after Massazza.<sup>[10,11]</sup> Yamaguchi<sup>[21]</sup> described a sol-gel synthesis of 12SrO · 7Al<sub>2</sub>O<sub>3</sub>, homologous with 12CaO · 7Al<sub>2</sub>O<sub>3</sub>,

crystallizing at 840-900 °C but decomposing at higher temperature into  $3\text{SrO} \cdot \text{Al}_2\text{O}_3$  and  $\text{SrO} \cdot \text{Al}_2\text{O}_3$ . Recently, Kahlenberg<sup>[22]</sup> found single crystals of  $10\text{SrO} \cdot 3\text{Al}_2\text{O}_3$  on the surface of strontium-rich pellets sintered at 1600 °C for 144 h.

In the present optimization, data on invariant equilibria and liquidus data from Ganits et al.<sup>[14]</sup> were mainly used. In their work,  $4\text{SrO} \cdot \text{Al}_2\text{O}_3$  occurred with a  $\beta$  form between 1403 and 1723 K and an  $\alpha$  form between 1723 and 2073 K. The reported homogeneity range of  $4\text{SrO} \cdot \text{Al}_2\text{O}_3$ <sup>[14]</sup> is not taken into account in the present work because of large uncertainties. For  $\text{SrO} \cdot \text{Al}_2\text{O}_3$ , a phase transformation at 932 K was taken into account during optimization; this has not been shown in published phase diagrams but was proven to exist.<sup>[23]</sup> Because the compound  $4\text{SrO} \cdot 7\text{Al}_2\text{O}_3$  was not found by Massazza,<sup>[10,11]</sup> nor Ganits et al.,<sup>[14]</sup> and is questioned by results of more recent research of Zhang et al.,<sup>[24]</sup> plus the fact that the compositions of  $4\text{SrO} \cdot 7\text{Al}_2\text{O}_3$  and  $\text{SrO} \cdot 2\text{Al}_2\text{O}_3$  are very close, the formula  $\text{SrO} \cdot 2\text{Al}_2\text{O}_3$  was used instead of  $4\text{SrO} \cdot 7\text{Al}_2\text{O}_3$  in present work. The new compounds  $14\text{SrO} \cdot 7\text{Al}_2\text{O}_3$  and  $10\text{SrO} \cdot 3\text{Al}_2\text{O}_3$  were also not included in the optimization because their stabilities are quite uncertain and are questioned by the work of André et al.<sup>[20]</sup>

## 2.2 Melting Point of End Member Compounds

The melting temperatures of  $\text{SrO}$  and  $\text{Al}_2\text{O}_3$  have been measured by many authors. However, there are large discrepancies among the published results. For  $\text{Al}_2\text{O}_3$ , 2327 K is selected since it was widely accepted. And for  $\text{SrO}$ , 2870 K is adopted in this work in accordance with the assessment of Risold et al.,<sup>[25]</sup> the lattice stabilities from the 1994 SGTE report<sup>[26]</sup> for pure  $\text{SrO}$  were modified accordingly.

## 2.3 Thermodynamic Properties

The thermodynamic data for the  $\text{Al}_2\text{O}_3$ - $\text{SrO}$  system are very scarce. Brisi et al.<sup>[12]</sup> measured the heat of formation of  $\text{SrO} \cdot \text{Al}_2\text{O}_3$ ,  $3\text{SrO} \cdot \text{Al}_2\text{O}_3$ , and  $4\text{SrO} \cdot \text{Al}_2\text{O}_3(\alpha)$  from oxides. Knacke et al.<sup>[23]</sup> have compiled the thermochemical properties of  $\text{SrO} \cdot \text{Al}_2\text{O}_3$ . The Gibbs energy expression for compounds  $\text{SrO} \cdot \text{Al}_2\text{O}_3$ ,  $3\text{SrO} \cdot \text{Al}_2\text{O}_3$ , and  $4\text{SrO} \cdot \text{Al}_2\text{O}_3(\alpha)$  existed in the SGTE substance database. However, none of these were used directly in the optimization because of the disparity of these data but were used as reference data to estimate the enthalpy of formation of these compounds. Capron et al.<sup>[27]</sup> investigated the local structure and dynamics of high temperature  $\text{SrO-Al}_2\text{O}_3$  liquids studied by <sup>27</sup>Al NMR and Sr K-edge XAS spectroscopy; the results indicated that the Al co-ordination number decreased from typically  $4.7 \pm 0.3$  in  $\text{Al}_2\text{O}_3$  liquid down to 4.0 for the liquids with the highest  $\text{SrO}$  contents; to some extent this satisfies the condition of the newly proposed model for  $\text{Al}_2\text{O}_3$ -involved liquid phase.<sup>[2]</sup> In their study, the melting points of the definite compounds were also tabulated, however, the origin of this value was untraceable and not included in the optimization. Also, owing to the experimental difficulties of high-temperature measurements, the mixing enthalpy of the  $\text{Al}_2\text{O}_3$ - $\text{SrO}$  melt is not available.

## 3. Modeling

### 3.1 Reference State

As reference states for the quasi-binary system, the pure elements in their stable states at 298.15 K (Stable Element Reference, SER) were chosen. The temperature dependence of the component compounds is given in the form:

$${}^0G_{i-\phi}(T) = a + bT + cT \ln T + dT^2 + e/T + fT^3 \quad \text{J/mol} \quad (\text{Eq 1})$$

where  ${}^0G_{i-\phi}(T)$  is the molar Gibbs energy of phase  $\phi$  of compound  $i$  at temperature  $T(\text{K})$ . In different temperature ranges, different sets of the coefficients  $a$  to  $f$  can be used.

### 3.2 Intermediate Phases

Intermediate phases, i.e.,  $\text{SrO} \cdot 6\text{Al}_2\text{O}_3$ ,  $\text{SrO} \cdot 2\text{Al}_2\text{O}_3$ ,  $\text{SrO} \cdot \text{Al}_2\text{O}_3$ ,  $3\text{SrO} \cdot \text{Al}_2\text{O}_3$  and  $4\text{SrO} \cdot \text{Al}_2\text{O}_3$  are modeled as stoichiometric phases. Taking  $\text{SrO} \cdot 6\text{Al}_2\text{O}_3$  as an example, the Gibbs energy for such solid state is given by following equation:

$${}^0G_{\text{SrO} \cdot 6\text{Al}_2\text{O}_3}(T) = G_{\text{SrO-S}}(T) + 6G_{\text{Al}_2\text{O}_3\text{-S}}(T) + a_{\text{SrO} \cdot 6\text{Al}_2\text{O}_3} + b_{\text{SrO} \cdot 6\text{Al}_2\text{O}_3}T \quad (\text{Eq 2})$$

### 3.3 Liquid Phase

A two-sublattice model for ionic solutions developed by Hillert et al.<sup>[28]</sup> was employed to successfully deal with the liquid phase of the  $\text{Al}_2\text{O}_3$ - $\text{MgO}$ ,<sup>[29]</sup> and  $\text{Al}_2\text{O}_3$ - $\text{CaO}$ <sup>[30]</sup> systems. To reflect the features of the local structure of a given liquid phase, it is most important to find a suitable model formula for the system. Recently, Mao et al.<sup>[2]</sup> introduced the species  $\text{AlO}_2^-$  into the liquid phase in the  $\text{Al}_2\text{O}_3$ - $\text{CaO}$  and  $\text{Al}_2\text{O}_3$ - $\text{MgO}$  systems in order to represent the  $\text{SiO}_2$ -like tetrahedral network for  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ -containing liquids; existence of such a network is supported by recent molecular dynamic (MD) simulations<sup>[31]</sup> and nuclear magnetic resonance (NMR) experiments.<sup>[32]</sup> The re-assessments fit all experimental information very well and improve the thermodynamic assessments of  $\text{CaO-Al}_2\text{O}_3$ - $\text{SiO}_2$ <sup>[33]</sup> and  $\text{MgO-Al}_2\text{O}_3$ - $\text{SiO}_2$ <sup>[34]</sup> additionally. In view of the structural similarity the binary pairs of systems  $\text{Al}_2\text{O}_3$ - $\text{BaO}$ ,  $\text{Al}_2\text{O}_3$ - $\text{SrO}$ , and  $\text{Al}_2\text{O}_3$ - $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ - $\text{MgO}$ , the new model should be suitable to deal with the  $\text{Al}_2\text{O}_3$ - $\text{BaO}$  and  $\text{Al}_2\text{O}_3$ - $\text{SrO}$  systems. The idea has been proven correct in the work of  $\text{Al}_2\text{O}_3$ - $\text{BaO}$ ,<sup>[3]</sup> furthermore, the work of Capron et al.<sup>[27]</sup> has confirmed the coordination number for  $\text{Al}_2\text{O}_3$  is four in the liquid phase of  $\text{Al}_2\text{O}_3$ - $\text{SrO}$ ; therefore, the modified model mentioned above was applied in present work. The liquid phase in the  $\text{Al}_2\text{O}_3$ - $\text{SrO}$  system can be described by the formula  $(\text{Al}^{3+}, \text{Sr}^{2+})_P (\text{AlO}_2^-, \text{O}^{2-})_Q$ , where  $P$  and  $Q$  represent the number of cation and anion sites, which vary with composition:

$$P = \sum y_i(\gamma_i) = y_{\text{AlO}_2^-} + 2y_{\text{O}^{2-}} \quad (\text{Eq 3})$$

$$Q = \sum y_j(\gamma_j) = 3y_{\text{Al}^{3+}} + 2y_{\text{Sr}^{2+}} \quad (\text{Eq 4})$$

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where  $\gamma_i$  and  $y_i, \gamma_j$  and  $y_j$  indicate the charges and site fractions of anion  $i$  and cation  $j$ , respectively. The Gibbs energy of the liquid phase is expressed as:

$$\begin{aligned} G_m = & y_{Al^{3+}} y_{AlO_2^{1-}} {}^0G_{Al^{3+}:AlO_2^{1-}} + y_{Al^{3+}} y_{O^{2-}} {}^0G_{Al^{3+}:O^{2-}} \\ & + y_{Sr^{2+}} y_{AlO_2^{1-}} {}^0G_{Sr^{2+}:AlO_2^{1-}} + y_{Sr^{2+}} y_{O^{2-}} {}^0G_{Sr^{2+}:O^{2-}} \\ & + PRT(y_{Al^{3+}} \ln y_{Al^{3+}} + y_{Sr^{2+}} \ln y_{Sr^{2+}}) \\ & + QRT(y_{AlO_2^{1-}} \ln y_{AlO_2^{1-}} + y_{O^{2-}} \ln y_{O^{2-}}) + {}^E G_m \end{aligned} \quad (\text{Eq 5})$$

${}^0G_{Al^{3+}:AlO_2^{1-}}$  and  ${}^0G_{Sr^{2+}:O^{2-}}$  are equal to the Gibbs energy of two moles of pure liquid  $Al_2O_3$  ( ${}^0G_{Al_2O_3,L}$ ) and two moles of pure liquid  $SrO$  ( ${}^0G_{SrO,L}$ ), respectively, which are taken from the SGTE substance database with some modification as mentioned above. In order to prevent the  $AlO_2^{1-}$  from dissociating into  $Al^{3+}$  and  $O^{2-}$  ions causing the pure liquid  $Al_2O_3$  to become unstable, the following equation is needed:

$${}^0G_{Al^{3+}:O^{2-}} = {}^0G_{Al_2O_3,L} + E \quad (\text{Eq 6})$$

Here the constant  $E$  has a large positive value. The value for  $E$  in the present optimization was taken from the work on  $Al_2O_3$ -CaO or  $Al_2O_3$ -MgO systems,<sup>[2]</sup> which seems quite reasonable. The  ${}^0G_{Sr^{2+}:AlO_2^{1-}}$  can be described by

$${}^0G_{Sr^{2+}:AlO_2^{1-}} = {}^0G_{Al_2O_3,L} + {}^0G_{SrO,L} + F \quad (\text{Eq 7})$$

where  $F$  is a parameter (in this case, a temperature term is added to obtain better results) to be assessed. The excess Gibbs energy term in Eq. (5),  ${}^E G_m$  is the function of the interaction between the species within each sublattice and described by Redlich-Kister polynomial<sup>[35]</sup> as follows.

$$\begin{aligned} {}^E G_m = & y_{Al^{3+}} y_{Sr^{2+}} y_{AlO_2^{1-}} {}^0L + y_{Sr^{2+}} y_{AlO_2^{1-}} y_{O^{2-}} \\ & [{}^0M + {}^1M(y_{AlO_2^{1-}} - y_{O^{2-}})] \end{aligned} \quad (\text{Eq 8})$$

where the interaction terms  $Al^{3+}$ ,  $Sr^{2+}:O^{2-}$  and  $Al^{3+}:AlO_2^{1-}$ ,  $O^{2-}$  were neglected because of the large  $E$  in Eq. (6).

**Table 1 Thermodynamic parameters of the  $Al_2O_3$ -SrO system, J/mol of formula units**

### Liquid

$$\begin{aligned} {}^0G_{Al^{3+}:AlO_2^{1-}} - 4H_{Al}^{SER} - 6H_O^{SER} &= 2{}^0G_{Al_2O_3,L} \\ {}^0G_{Sr^{2+}:AlO_2^{1-}} - 2H_{Sr}^{SER} - 4H_O^{SER} &= {}^0G_{SrO,L} + {}^0G_{Al_2O_3,L} - 246192 + 65.049T \\ {}^0G_{Al^{3+}:O^{2-}} - 2H_{Al}^{SER} - 3H_O^{SER} &= {}^0G_{Al_2O_3,L} + 900000 \\ {}^0G_{Sr^{2+}:O^{2-}} - 2H_{Sr}^{SER} - 2H_O^{SER} &= 2{}^0G_{SrO,L} \\ {}^1L_{Al^{3+},Sr^{2+}:AlO_2^{1-}} &= -294360 + 106.975T \\ {}^0M_{Sr^{2+}:AlO_2^{1-},O^{2-}} &= -259611 + 85.404T \\ {}^1M_{Sr^{2+}:AlO_2^{1-},O^{2-}} &= 70281 \end{aligned}$$

### Intermediate compounds

$$\text{SrO} \cdot 6Al_2O_3$$

$${}^0G_{6Al_2O_3:SrO} = 6{}^0G_{Al_2O_3,S} + {}^0G_{SrO,S} - 110494$$

$$\text{SrO} \cdot 2Al_2O_3$$

$${}^0G_{6Al_2O_3:SrO} = 2{}^0G_{Al_2O_3,S} + {}^0G_{SrO,S} - 102255$$

$$\text{SrO} \cdot Al_2O_3$$

$$\text{H} :$$

$${}^0G_{Al_2O_3:SrO} = {}^0G_{Al_2O_3,S} + {}^0G_{SrO,S} - 79200(932 < T < 2233)$$

$$:$$

$${}^0G_{Al_2O_3:SrO} = {}^0G_{Al_2O_3,S} + {}^0G_{SrO,S} - 81124.6 + 2.065^*T(298.15 < T < 932)$$

$$3\text{SrO} \cdot Al_2O_3$$

$${}^0G_{Al_2O_3:3SrO} = {}^0G_{Al_2O_3,S} + 3{}^0G_{SrO,S} - 109962$$

$$4\text{SrO} \cdot Al_2O_3$$

$$\alpha :$$

$${}^0G_{Al_2O_3:3SrO} = {}^0G_{Al_2O_3,S} + 4{}^0G_{SrO,S} - 100667 - 6.3963T$$

$$\beta :$$

$${}^0G_{Al_2O_3:3SrO} = {}^0G_{Al_2O_3,S} + 4{}^0G_{SrO,S} - 102390 - 5.3963T$$

### Functions

$${}^0G_{Al_2O_3,L}(298.15 < T < 4000.00) = {}^0G_{Al_2O_3,S} + 111085.2 - 47.7375161T$$

$${}^0G_{Al_2O_3,S}(298.15 < T < 600.00) = -1707353.3 + 448.02120T - 67.48039T \ln T - 0.06746995T^2 + 1.42054467 \times 10^{-5}T^3 + 938781T^{-1}$$

$${}^0G_{Al_2O_3,S}(600.00 < T < 1500.00) = -1724888.03 + 754.856079T - 116.2579T \ln T - 0.007225685T^2 + 2.78531667 \times 10^{-7}T^3 + 2120702T^{-1}$$

$${}^0G_{Al_2O_3,S}(1500.00 < T < 2327.00) = -1772165.64 + 1053.45681T - 156.0582T \ln T + 0.007091065T^2 - 6.29401833 \times 10^{-7}T^3 + 12366670T^{-1}$$

$${}^0G_{SrO,L}(298.15 < T < 5000.00) = {}^0G_{SrO,S} + 89410 - 31.1533101T$$

$${}^0G_{SrO,S}(298.15 < T < 900.00) = -607329.171 + 252.319465T - 44.96126T \ln T - 0.00826347T^2 + 8.58696333 \times 10^{-7}T^3 + 178730T^{-1}$$

$${}^0G_{SrO,S}(900.00 < T < 2870.00) = -609963.764 + 287.955734T - 50.37118T \ln T - 0.003286532T^2 + 3.136675 \times 10^{-9}T^3 + 426014.9T^{-1}$$

**Table 2** Calculated and experimental invariant temperatures and compositions for the  $\text{Al}_2\text{O}_3$ -SrO binary system

Reaction	Temperature (K)	Liquid composition (mol% $\text{Al}_2\text{O}_3$ )	Reference	Type
$\text{L} + \text{Al}_2\text{O}_3 = \text{SrO} \cdot 6\text{Al}_2\text{O}_3$	2067	0.776	This work	Peritectic
	2063	0.858	[14]	
	2233 <sup>a</sup>	0.857 <sup>a</sup>	[26]	
$\text{L} \leftrightarrow \text{SrO} \cdot 6\text{Al}_2\text{O}_3 + \text{SrO} \cdot 2\text{Al}_2\text{O}_3$	1977	0.728	This work	Eutectic
	1983	0.733	[14]	
	2053	0.742	[10]	
$\text{L} \leftrightarrow \text{SrO} \cdot 2\text{Al}_2\text{O}_3$	2053	0.666	This work	Congruent point
	2053	0.666	[14]	
	2103	0.666	[26]	
$\text{L} \leftrightarrow \text{SrO} \cdot 2\text{Al}_2\text{O}_3 + \text{H-SrO} \cdot \text{Al}_2\text{O}_3$	1937	0.596	This work	Eutectic
	1933	0.584	[14]	
	2033	0.58	[10]	
$\text{L} \leftrightarrow \text{H-SrO} \cdot \text{Al}_2\text{O}_3$	2233	0.50	This work	Congruent point
	2233	0.50	[14]	
	2063	0.50	[10]	
	2288	0.50	[26]	
$\text{H-SrO} \cdot \text{Al}_2\text{O}_3 \leftrightarrow \text{L-SrO} \cdot \text{Al}_2\text{O}_3$	932		This work	Phase transformation
	932		[23]	
$\text{L} \leftrightarrow \text{SrO} \cdot \text{Al}_2\text{O}_3 + 3\text{SrO} \cdot \text{Al}_2\text{O}_3$	1830	0.356	This work	Eutectic
	1833	0.330	[14]	
	1778	0.326	[10]	
$\text{L} \leftrightarrow 3\text{SrO} \cdot \text{Al}_2\text{O}_3$	2005	0.25	This work	Congruent point
	2009	0.25	[14]	
	1933	0.25	[10, 11]	
	2093	0.25	[26]	
$\text{L} \leftrightarrow 3\text{SrO} \cdot \text{Al}_2\text{O}_3 + \alpha\text{-4SrO} \cdot \text{Al}_2\text{O}_3$	2004	0.244	This work	Eutectic
	1960	0.238	[14]	
	1903	0.235	[10, 11]	
$\text{L} + \text{SrO} \leftrightarrow \alpha\text{-4SrO} \cdot \text{Al}_2\text{O}_3$	2038	0.216	This work	Peritectic
	2073	0.194	[14]	
	1963	0.210	[10, 11]	
	2153 <sup>a</sup>	0.20 <sup>a</sup>	[26]	
$\alpha\text{-4SrO} \cdot \text{Al}_2\text{O}_3 \leftrightarrow \beta\text{-4SrO} \cdot \text{Al}_2\text{O}_3$	1723		This work	Phase transformation
	1723		[14]	
	1593		[10, 11]	
$\beta\text{-4SrO} \cdot \text{Al}_2\text{O}_3 \leftrightarrow \text{SrO} + 3\text{SrO} \cdot \text{Al}_2\text{O}_3$	1403		This work	Phase transformation
	1403		[14]	
	1398		[10, 11]	

<sup>a</sup>The values of stoichiometric compounds

#### 4. Optimization

The optimization was performed using the PARROT module of the Thermo-calc software package.<sup>[36]</sup>

First, the enthalpy of formation of  $\text{SrO} \cdot \text{Al}_2\text{O}_3$  at high temperature ( $> 932$  K, marked as  $\text{H-SrO} \cdot \text{Al}_2\text{O}_3$ ) was estimated as  $-79.2$  kJ/mol by comprehensive consideration of the values from Brisi et al.,<sup>[12]</sup> Kubaschewski et al.,<sup>[23]</sup> and SGTE database. The Gibbs energy of  $\text{SrO} \cdot \text{Al}_2\text{O}_3$  at low temperature ( $< 932$  K,  $\text{L-SrO} \cdot \text{Al}_2\text{O}_3$ ) was obtained by adding the Gibbs free energy expression of phase transformation ( $-1924 + 2.065 \times T$ ) from Kubaschewski et al.,<sup>[23]</sup> which is the same as SGTE database.

Then all other solid phases were fitted to experimental data. The entropy of phase transformation  $\beta \rightarrow \alpha$  of  $4\text{SrO} \cdot \text{Al}_2\text{O}_3$  was estimated as a reasonably small value of 1 J/mol per Kelvin by considering the solid-state transformation between two close-packed polymorphic forms. Then the enthalpy of phase transformation was given out based on the transformation temperature and the value of entropy.

Next, the parameters for the liquid phase were optimized.

Finally, all experimental information was included and the optimization repeated until a satisfactory description of most experimental data was reached. All equilibria were calculated using the POLY-3 module included in the

**Table 3 Heat of formation from oxides at 298.15 K for the strontium aluminates**

	Phase			
	SrO · Al <sub>2</sub> O <sub>3</sub>	3SrO · Al <sub>2</sub> O <sub>3</sub>	4SrO · Al <sub>2</sub> O <sub>3</sub> (β)	4SrO · Al <sub>2</sub> O <sub>3</sub> (α)
Present work	-79.2	-109.9	-104.0	-102.6
Brisi et al. <sup>[12]</sup>	-79.2 ± 2.9	-97.7 ± 4.2	-92.7 ± 5.0	-81.4 ± 5.4
Kubaschewski et al. <sup>[13]</sup>	-71.128	...	...	...

**Table 4 The melting characteristics of intermediate compounds of Al<sub>2</sub>O<sub>3</sub>-AEO (AE = Mg, Ca, Sr)**

System	Intermediate phases	T <sub>fus</sub> <sup>0</sup> (K)	
		Cal.	Exp. <sup>b</sup>
Al <sub>2</sub> O <sub>3</sub> -MgO	MgO · Al <sub>2</sub> O <sub>3</sub> (Stoichiometric spinel)	2378	2408, 2378
Al <sub>2</sub> O <sub>3</sub> -CaO	3CaO · Al <sub>2</sub> O <sub>3</sub>	1817 <sup>a</sup>	1814, 1808
	CaO · Al <sub>2</sub> O <sub>3</sub>	1874	1874, 1873, 1878
	CaO · 2Al <sub>2</sub> O <sub>3</sub>	2050	1993, 2018, 2023
	CaO · 6Al <sub>2</sub> O <sub>3</sub>	2156	2106, 2093, 2148, 2133, 2123
Al <sub>2</sub> O <sub>3</sub> -SrO	4SrO · Al <sub>2</sub> O <sub>3</sub> (α)	2038 <sup>a</sup>	2073, 1963, 2153
	3SrO · Al <sub>2</sub> O <sub>3</sub>	2005	2009, 1933, 2093
	SrO · Al <sub>2</sub> O <sub>3</sub>	2233	2238, 2063, 2288
	SrO · 2Al <sub>2</sub> O <sub>3</sub>	2053	2053, 2103
	SrO · 6Al <sub>2</sub> O <sub>3</sub>	2067 <sup>a</sup>	2063, 2233

<sup>a</sup>Decomposition temperature

<sup>b</sup>The experimental data for MgO and CaO-Al<sub>2</sub>O<sub>3</sub> systems were taken from the assessed work of Hallstedt,<sup>[28, 29]</sup> for SrO-Al<sub>2</sub>O<sub>3</sub> system, details can be found in Table 2

Thermo-Calc package system. The parameters of all phases are listed in Table 1.

## 5. Results and Discussions

The calculated phase diagram compared with all available experimental data<sup>[10, 11, 14, 26]</sup> is shown in Fig. 1, and the evaluated values for the invariant temperatures and liquid compositions are listed in Table 2. The calculated heats of formation of intermediate compounds from end-member oxides are compared with experimental ones in Table 3. Figure 2 demonstrates the mixing enthalpy of Al<sub>2</sub>O<sub>3</sub>-SrO in the melt, as well as Al<sub>2</sub>O<sub>3</sub>-MgO,<sup>[2]</sup> and Al<sub>2</sub>O<sub>3</sub>-CaO<sup>[2]</sup> (referred to liquid Al<sub>2</sub>O<sub>3</sub> and AEO (AE = Mg, Ca)).

As shown in the Fig. 1 and Table 2, the calculated phase boundaries generally agree well with the experimental data,<sup>[14]</sup> which indicates that it is reasonable to use the ionic two-sublattice model (Al<sup>3+</sup>, Sr<sup>2+</sup>)<sub>P</sub> (AlO<sub>2</sub><sup>1-</sup>, O<sup>2-</sup>)<sub>O</sub> to describe the liquid phase. Compared with the measured data, the liquidus near SrO is not fitted well, which is partially due to the higher melting point of 2870 K for SrO<sup>[25]</sup> used in this study instead of 2703 K in the phase diagram measured by Ganits et al.<sup>[14]</sup> As can be seen from Table 3, the calculated heats of formation of the intermediate compounds at 298.15 K agree with the experimental data<sup>[12]</sup>. However, apart from these better reproduction, it should be pointed out that the temperature terms for liquid

phase look increasingly positive with increasing temperature and this may result in an inverted miscibility gap at elevated temperatures above 3300 K. An effort was made to get rid of the inverse miscibility gap but failed. When the parameters for the intermediate compounds are one order greater in magnitude than those of the present study, it seems possible the miscibility gap would be removed. But this is obviously inauthentic. An explanation possible for this is that the modified Gibbs function for the SrO and Al<sub>2</sub>O<sub>3</sub> liquid phases is no longer reliable at very high temperature. Therefore, the calculated properties for the liquid phase cannot be trusted above 3300 K. Also due to the lack of experimental evidence, the parameters for SrO · 6Al<sub>2</sub>O<sub>3</sub> and SrO · 2Al<sub>2</sub>O<sub>3</sub> (Table 1) should be considered as tentative. More reliable values can be obtained only from further experimental studies.

The predicted enthalpy of mixing at 3200 K of the Al<sub>2</sub>O<sub>3</sub>-SrO system is indicated in the Fig. 2, as well as the calculated results of similar systems of Al<sub>2</sub>O<sub>3</sub>-MgO, Al<sub>2</sub>O<sub>3</sub>-CaO. From MgO to SrO, the mixing enthalpies (generally, can be considered as independent of temperature) show a reasonable trend and present a gradual decrease. But it should be pointed out that the mixing enthalpies of Al<sub>2</sub>O<sub>3</sub>-SrO exhibit more negative values than those of Al<sub>2</sub>O<sub>3</sub>-BaO.<sup>[3]</sup> It appears impossible to obtain a consistent phase diagram when reducing the absolute values of mixing enthalpies of Al<sub>2</sub>O<sub>3</sub>-SrO. Thus, further experimental work is needed to clarify this point in the future.



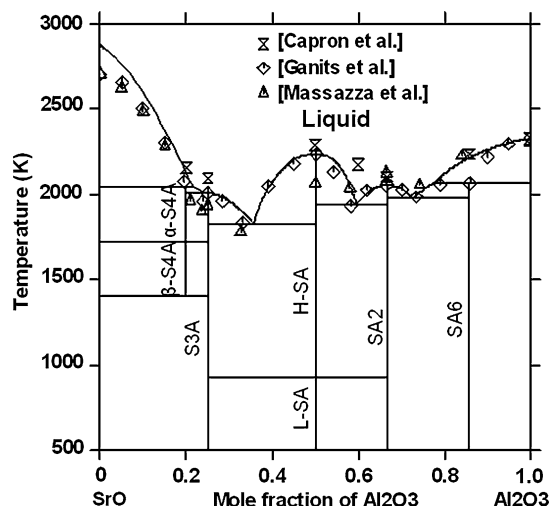


Fig. 1 Calculated phase diagram compared with experimental data (S = SrO, A = Al<sub>2</sub>O<sub>3</sub>)

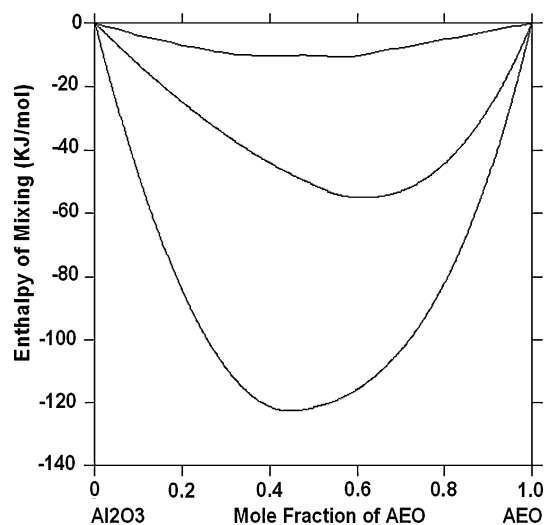


Fig. 2 Mixing enthalpy of Al<sub>2</sub>O<sub>3</sub>-AEO (AE = Mg, Ca, Sr) melt; from top to bottom, 3200 K for MgO-Al<sub>2</sub>O<sub>3</sub>, CaO-Al<sub>2</sub>O<sub>3</sub>, and SrO-Al<sub>2</sub>O<sub>3</sub>, respectively (the temperature for calculation is selected based on the temperature when the entire liquid occurred)

A summary of already assessed stable intermediate compounds existing in above three lighter alkaline earth aluminate systems is given in Table 4. The experimental and calculated melting (decomposition) points of these compounds are also tabulated. As shown in the table, there are more and more kinds of the intermediate compounds in order of MgO-Al<sub>2</sub>O<sub>3</sub>, CaO-Al<sub>2</sub>O<sub>3</sub>, SrO-Al<sub>2</sub>O<sub>3</sub> systems, this reflects and verifies the change of mixing enthalpy to some extent.

## 6. Conclusions

The phase diagram and thermodynamic properties of the Al<sub>2</sub>O<sub>3</sub>-SrO binary system are critically assessed in this

study. The liquid phase is modeled by the ionic two-sublattice model as (Al<sup>3+</sup>, Sr<sup>2+</sup>)<sub>P</sub>(AlO<sub>2</sub><sup>-</sup>, O<sup>2-</sup>)<sub>Q</sub>. The calculated results fit well with experimental ones. The enthalpy of mixing is predicted and compared with other similar systems. Also the number and melting points of intermediate compounds of similar systems are summarized. Further work may be needed to experimentally verify the results of the present work.

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