

## Calculation of Lattice Energies and Enthalpies of Formation of Rare-Earth Pyrosilicates

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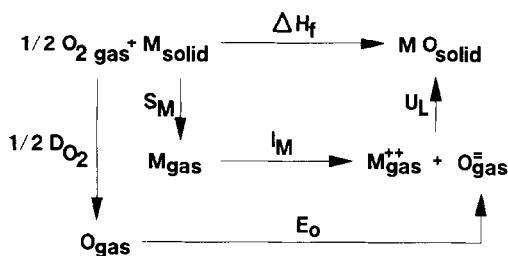
The lattice energies of ionic crystals were calculated from a computer summation of the Coulombic interaction energies. The present technique was first applied to simple crystal symmetries, including rock salts, fluorites, and silicates, to establish the reliability of the method. Calculated values for these systems were found to be within 3 to 8% of the accepted values. The lattice energies of several of the light rare-earth (La through Eu) pyrosilicates,  $\text{RE}_2\text{Si}_2\text{O}_7$ , were calculated by the same procedure. The enthalpies of formation for these crystals were then estimated from the calculated lattice energies by applying the Born–Haber cycle. Both the low temperature tetragonal and the high temperature orthorhombic forms of the pyrosilicates were calculated. © 1990 Academic Press, Inc.

### I. Introduction

In a previous study, it was shown that the addition of light rare-earth oxides to aluminosilicate refractory compositions improves their resistance to molten aluminum alloy attack (1). A microstructural study of this refractory system indicated that beta rare-earth pyrosilicates ( $\beta\text{-RE}_2\text{Si}_2\text{O}_7$ ) were the primary rare-earth compounds formed during firing of these compositions (2). There were no experimental thermodynamic data available for these silicates in the literature. In the present study the enthalpies of formation are calculated to assess whether the chemical stability of the pyrosilicate was responsible for the improved resistance of the rare-earth doped aluminosilicate refractories to aluminum alloy attack.

The Born–Haber cycle is frequently used to calculate either enthalpy of formation or lattice energy when the other is known (3). In this well-known technique, elemental species are taken from their standard states at a given temperature, evaporated to monatomic gases, ionized, reacted, and condensed to the crystalline state. Enthalpy of formation is equal to the algebraic sum of all the energies associated with the steps in this process. The Born–Haber cycle for a simple diatomic metal oxide is shown in Fig. 1. Unfortunately, neither the lattice energy nor the enthalpy are known for the rare-earth silicates. In order to calculate the enthalpies of formation of these silicates, the lattice energies must first be calculated from the known crystal structures.

Between 1918 and 1924, Madelung, Haber, Born and Lande developed the quanti-



$$\Delta H_f = U_L + I_M + E_o + S_M + 1/2 D_{\text{O}_2}$$

FIG. 1. The Born-Haber cycle for a simple diatomic metal oxide.  $H_f$  = enthalpy of formation,  $U_L$  = lattice energy,  $I_M$  = ionization potential of the metal,  $E_o$  = electron affinity of oxygen,  $S_M$  = sublimation energy of the metal,  $D_{\text{O}_2}$  = dissociation energy of oxygen.

tative theory of ionic crystals which is still used today. Born and Lande in particular were responsible for the formulas which allow the calculation of lattice energy and enthalpy of an ionic crystal from the interaction of individual ion pairs (4). Since that time several researchers, such as Born and Mayer (5), Kapustinskii (6), and Kapustinskii and Yatsimirskii (7), have modified the form of the lattice energy equation and the inherent assumptions. Ewald (8) developed a more rapidly converging method of calculating the electrostatic potential in a crystal structure composed of point charges.

## II. Approach

In this work, a simple summation, similar to that of the Madelung constant calculation, was used. The three-dimensional coordinates of the special positions of ions in complex crystals and their space group symmetries were taken from literature. Using symmetry operations on the special ion positions, the coordinates of all of the ions in the unit cell were generated. Larger multicell crystals were then constructed by stacking cells along the crystallographic

axes. The Coulombic attractions and repulsions of every ion were summed with respect to all the other ions in the crystal. From this sum and other constant terms, the lattice energy was then calculated using

$$U = \frac{Ne^2}{8\pi\epsilon_0} \left( 1 - \frac{1}{n} \sum_i \sum_j \frac{Z_i Z_j}{R_{ij}} \right), \quad i \langle \rangle j, \quad (1)$$

where

$U$  = lattice energy (finite crystal)

$Z_i$  = valence of ion  $i$

$Z_j$  = valence of ion  $j$

$R_{ij}$  = distance between ions  $i$  and  $j$

$\epsilon_0$  = permittivity of free space

$n$  = Born exponent

$e$  = charge on an electron

$N$  = Avagadro's number.

Here, the Born repulsion term is taken outside of the summation similar to the Madelung expression.

## III. Procedure

The lattice energies of simple rock salt and fluorite structure crystals were calculated in order to establish the reliability of the method and to determine the level of errors. For all of the crystal systems a computer program was used to calculate the summation in Eq. (1). Once the lattice energies of simple ionic structures were confirmed, less ionic and more structurally complex crystals were calculated before proceeding to the unknown rare-earth silicates. The lattice energies of  $\beta$ -quartz and  $\alpha$ - $\text{Na}_2\text{Si}_2\text{O}_5$  were included because of their similarities to the rare-earth silicate systems. The lattice constants, special ion positions, and the space groups of the crystal systems were obtained from literature as shown in Table I.

From the special ion positions and the space group data, the locations of atoms in the cells of crystals were generated using equivalent position symmetry operations from the *International Tables* (14).

TABLE I  
CRYSTAL STRUCTURES AND LATTICE PARAMETERS

Crystal	Symmetry	Lattice parameters			Reference
		$a_0$	$b_0$	$c_0$	
NaCl	Rock salt	5.64056			Wyckoff (9)
CaF <sub>2</sub>	Fluorite $Fm\bar{3}m$	5.46295			Wyckoff (9)
SiO <sub>2</sub>	$\beta$ -Quartz Hex. $P6_22$	5.01		5.47	Wyckoff (9)
$\alpha$ -Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	$Pbnc$ , orthorhombic	6.409	15.422	4.896	Pant and Cruickshank (10)
Low RE pyrosilicates					
$\alpha$ -La <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	$P4_1$ ,	6.7945		24.871	Dago <i>et al.</i> <sup>a</sup> (11)
$\alpha$ -Pr <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	tetragonal	6.7657		24.608	Felsche and Hirsiger <sup>b</sup> (12)
$\alpha$ -Nd <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>		6.7405		24.524	
$\alpha$ -Sm <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>		6.6933		24.384	
High RE pyrosilicates					
$\beta$ -La <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	$P2_12_12_1$ ,	5.410	13.17	8.76	Smolin and Shepelev (13)
$\beta$ -Ce <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	orthorhombic	5.400	13.05	8.73	
$\beta$ -Nd <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>		5.394	12.95	8.72	
$\beta$ -Sm <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>		5.384	12.85	8.69	
$\beta$ -Eu <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>		5.374	12.82	8.65	

<sup>a</sup> Dago *et al.* provide special positions of ions.

<sup>b</sup> Felsche and Hirsiger give lattice parameters.

Simple computer programs were written to carry out the calculations. One program constructed crystals and recorded the three-dimensional coordinates of the ions. A second program summed the Coulombic attractions and repulsions of a particular three-dimensional network of ions.

Prior to and during cell stacking, ionic space coordinates were defined by the crystallographic axes of the particular structure. Consequently, after cell stacking, those crystal symmetries defined by other than orthogonal axes were transformed to Cartesian coordinates by the computer program. For example,  $\beta$ -quartz is defined by hexagonal ion coordinates. Furthermore, cell stacking must be done along hexagonal directions in order to maintain the continuity of the structure. After stacking, however, the Cartesian coordinates of all ions were generated regardless of the symmetry of the original crystal.

The Coulombic interaction was calculated for ions  $j$  and  $k$  by first establishing the distance between them in Angstroms. In Cartesian coordinates, this distance is simply the square root of the sum of the squares of the coordinate differences. The Coulombic contribution for each  $j-k$  pair was calculated according to the appropriate charges of the  $j$  and  $k$  ions as shown in Eq. (1). A running summation was made of all of the interactions, resulting in a total Coulombic energy for a given lattice of ions.

Starting with single cells and progressing to several hundred cells, Coulomb energy summations were computed for crystals of increasing size. As shown in Fig. 2, as the number of formula units in a crystal increases, the lattice energy per mole asymptotically approaches a lower limit. The value of this asymptote is the predicted value of the lattice energy of an infinite crystal. This asymptote can be unambigu-

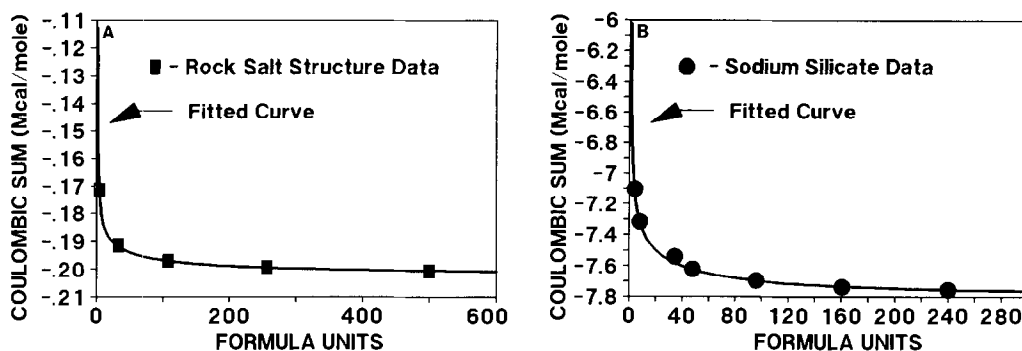


FIG. 2. Coulombic energy data and fitted curves are displayed for (A) NaCl and (B)  $\alpha$ - $\text{Na}_2\text{Si}_2\text{O}_5$ .

ously evaluated by nonlinear least-squares fitting of these data to a generalized asymptotic equation. After trying numerous more simple equations, the following hyperbolic form was chosen:

$$y(x) = A + \frac{B}{x} + C \log_e \frac{1 + \sqrt{1 + (x + D)^2}}{(x + D)}. \quad (2)$$

The fitted parameter  $A$  is the value of the  $y$ -axis asymptote and is the predicted lattice energy of an infinite crystal.

## IV. Results and Discussion

### IV.A. Coulombic Summations and Lattice Energies

Coulombic summations asymptotically approached a negative limit as the crystal size increased. In Table II, the Coulombic summation energies and the corresponding crystal size in number of formula units are tabulated. The relationship between crystal size and Coulombic sum is illustrated in Fig. 2 for a high symmetry rock salt crystal and the more complex silicate ( $\alpha$ - $\text{Na}_2\text{Si}_2\text{O}_5$ ). In addition to the raws data points shown, a nonlinear regression curve for each crystal is also plotted in Fig. 2. Note that the fit for ( $\alpha$ - $\text{Na}_2\text{Si}_2\text{O}_5$ ) is not quite as good as that for the cubic structure. This is the result of

lower symmetry and corresponding variations in the stacking of cells. Cubic cells can be easily stacked to minimize surface energy for a particular crystal volume. Note that the number of formula units of the cubic data points usually corresponds to equiaxed crystals. The lattice constants of the silicate (orthorhombic) crystal are 6.4, 15.4, and 4.9. Cell stacking causes variations in the ratio of volume to surface. When this ratio is relatively low for a particular number of formula units, the data point falls above the curve or further away from the asymptote. This problem is also demonstrated in the standard deviation data provided in Table II.

The calculated lattice energies were in reasonable agreement with the accepted values. In Table III, a comparison is given between the lattice energies calculated from this lattice summation, from known Madelung constants, and from the Born-Haber cycle. For the ionic NaCl and  $\text{CaF}_2$  crystals, correlation is good. Several higher valence ionic compounds, such as  $\text{CeO}_2$  and MgO, having fluorite or rock salt structure were also calculated with similar results, as expected.

Data for  $\beta$ -quartz in Table II show good agreement for a covalently bonded crystal. Note also that convergence occurs more slowly than the cubic systems described earlier. This was at least partially antici-

TABLE II  
COULOMBIC INTERACTION SUMMATION ENERGIES

Formula units	Coulombic interaction energy (kcal/mole)					
	NaCl	CaF <sub>2</sub>	$\beta$ -Quartz	$\alpha$ -Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	$\alpha$ -La <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	$\beta$ -La <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>
1						-8,695.31
2					-9,696.87	
3			-3022.51			
4	-171.51	-469.97		-7107.74		-9,160.58
8				-7317.23	-9975.18	
24			-3136.22	-7534.20		-9,629.98
32	-191.85	-576.06			-10,271.15	
48				-7623.75		-9,814.75
72					-10,355.87	
81			-3213.84			
96				-7695.56		
108	-197.12	-618.21				
120						-10,004.61
128					-10,384.32	
160				-7740.50		
192			-3260.77			-10,070.06
240				-7756.56		
256	-199.49	-639.82				
375			-3289.18			
500	-200.72	-651.87				
648			-3302.78			
A <sup>a</sup>	-202.16	-666.28	-3325.52	-7806.68	-10,428.64	-10,197.33
Std. Dev.	0.0596	0.6971	1.1695	4.6439	2.3771	1.9699

<sup>a</sup> Obtained from nonlinear regression curve fitting. The value of A corresponds to the Coulomb energy at an infinite number of formula units.

TABLE III  
LATTICE ENERGY CALCULATIONS AND COMPARISONS

Crystal	Born exp., <i>n</i>	Lattice energy <sup>a</sup> (kcal/mole)			% Error <sup>b</sup>	
		-U <sub>L</sub>	-U <sub>M</sub>	-U <sub>BH</sub>	E <sub>12</sub>	E <sub>13</sub>
NaCl	10	181.94	185.28	188.46	1.80	3.46
CaF <sub>2</sub>	9	592.25	628.99	629.56	5.84	5.92
$\beta$ -Quartz	9	2956.02	3236.83	3209.40	8.67	7.89
$\alpha$ -Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	9	6939.27	NA	7153.00	NA	3.00

<sup>a</sup> U<sub>L</sub>, calculated from U<sub>L</sub> = A(1 - 1/n); U<sub>M</sub>, calculated from the known Madelung constant; and U<sub>BH</sub>, calculated from the Born-Haber cycle.

$$^b E_{12} = \left( \frac{U_M - U_L}{U_M} \right) \times 100, E_{13} = \left( \frac{U_{BH} - U_L}{U_{BH}} \right) \times 100.$$

pated because of the hexagonal symmetry. Cell stacking along hexagonal axes produces crystals that have lower volume to surface ratios than cubic crystals, hence, causing slower convergence. The agreement between the calculated and accepted lattice energy values is quite good. The Coulombic model is based upon an assumption that the crystal is ionic. The Coulombic energy is summed over a cloud of point charges in space. Considering the highly covalent nature of  $\beta$ -quartz, the error is smaller than anticipated.

The lattice energy for  $\alpha$ - $\text{Na}_2\text{Si}_2\text{O}_5$  is within 3% of the value calculated by the Born-Haber cycle. This silicate was chosen because of its structural and compositional similarity to the desired rare-earth silicates. It is thought to be representative of the approximate level of error in the RE-silicate calculations. Note that the present calculated lattice energies are all less negative than the accepted values, as shown in Table III. Hence, it is probable that the calculated lattice energies of the RE-silicates are also less negative than the actual values.

#### IV.B. Rare-Earth Pyrosilicates

The light rare-earths, La through Sm, form pyrosilicates of the chemical form  $\text{RE}_2\text{Si}_2\text{O}_7$ , having two structural polymorphs (10). The low temperature tetragonal structure is formed from the high temperature orthorhombic structure only through careful annealing. The Coulombic interaction data for low ( $\alpha$ ) and high ( $\beta$ ) lanthanum-pyrosilicate are tabulated in Table II. Lattice energy and enthalpy of formation values are shown for these polymorphs in Table IV. Note that the  $\alpha$ -pyrosilicate structure converged significantly more rapidly than the  $\beta$  polymorph. The  $\alpha$  form was within 0.6% of the asymptote at 72 formula units, while the high temperature structure was approximately 3% away. The  $\beta$ -structure converged more slowly because it has

TABLE IV  
LATTICE ENERGY AND ENTHALPIES OF FORMATION  
CALCULATIONS FOR CRYSTALS OF LOW ( $\alpha$ ) AND HIGH  
( $\beta$ ) RARE-EARTH PYROSILICATES

Crystal	Born exp., $n$	Lattice energy, <sup>a</sup> $-U_L$ (kcal/mole)	Enthalpy of formation, <sup>b</sup> $-H_f$ (kcal/mole)
$\alpha$ - $\text{La}_2\text{Si}_2\text{O}_7$	11	9480.58	834.90
$\alpha$ - $\text{Pr}_2\text{Si}_2\text{O}_7$	11	9587.43	859.71
$\alpha$ - $\text{Nd}_2\text{Si}_2\text{O}_7$	11	9622.31	875.83
$\alpha$ - $\text{Sm}_2\text{Si}_2\text{O}_7$	11	9686.08	897.60
$\beta$ - $\text{La}_2\text{Si}_2\text{O}_7$	11	9270.30	624.62
$\beta$ - $\text{Ce}_2\text{Si}_2\text{O}_7$	11	9315.60	637.26
$\beta$ - $\text{Nd}_2\text{Si}_2\text{O}_7$	11	9346.74	600.26
$\beta$ - $\text{Sm}_2\text{Si}_2\text{O}_7$	11	9387.99	599.51
$\beta$ - $\text{Eu}_2\text{Si}_2\text{O}_7$	11	9416.33	608.01

<sup>a</sup>  $U_L = A(1 - 1/n)$ , where  $A$  is the fitted parameter, see Table II.

<sup>b</sup> Calculated from the lattice energies using the Born-Haber cycle.

a more open structure and consequently more surface area per unit charge. The transformation from the  $\alpha$ - to  $\beta$ -structure results in an 8% decrease in density.

No low temperature form of cerium is tabulated. Though the structure should theoretically exist, previous researchers were not successful in creating  $\alpha$ -cerium pyrosilicate (12).

Within each structure the lattice energies become more negative as the atomic number of the rare-earth element increases, as shown in Fig. 3. The opposite trend would be anticipated from the electronegativity differences or the degree of ionicity of these silicates. However, this increase in lattice energy results from the well-known lanthanide contraction. In the low temperature pyrosilicates this increase in lattice energies is more pronounced than that in the high temperature structure. Lanthanide contraction in the low temperature form causes a greater change in the lattice energy because ions are closer together, analogous to solid spheres that are nearly touching. In the more open high temperature form, this contraction has less effect on the lattice en-

ergy. In addition, the opposing influence of relative ionicity may become significant in the higher temperature structure. The lattice energy difference between La to Sm is roughly 205 kcal/mole for the (low) tetragonal structure relative to 117 kcal/mole in the  $\beta$ -structure.

The enthalpies of formation also increase fairly uniformly in the low temperature structure, as shown in Fig. 4. However, the trend for the  $\beta$ -pyrosilicate enthalpies is more complex. Because of the relatively low ionization potentials of La and Ce, the enthalpies of formation of  $\beta$ -La and  $\beta$ -Ce pyrosilicate are more negative than those of Nd, Sm, and Eu. Excluding the lattice energies and ionization potentials, the other values in the Born-Haber cycles of these compounds are very similar.

The polymorphic transformation temperature has been reported as roughly 1600 K. The transformational enthalpies (differences between  $\alpha$  and  $\beta$  enthalpies of formation) are approximately 200 kcal/mole. Since the free energies of formation for  $\alpha$  and  $\beta$  are equal at the transformation temperature, the implied entropy of transformation is approximately 125 cal/mole. This entropy estimation appears reasonable. Be-

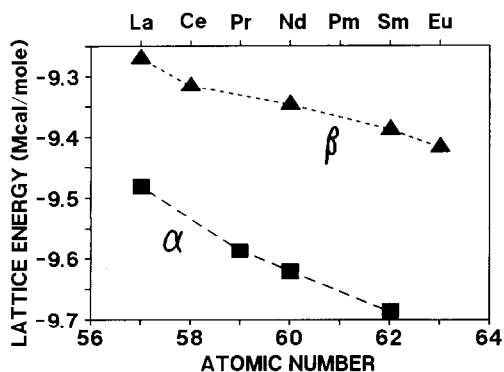


FIG. 3. Lattice energies from curve fitted data are shown for the light rare-earth  $\alpha$ - and  $\beta$ -pyrosilicates as a function of the atomic number ( $\alpha$ - $\text{RE}_2\text{Si}_2\text{O}_7$  = low temperature form,  $\beta$ - $\text{RE}_2\text{Si}_2\text{O}_7$  = high temperature form).

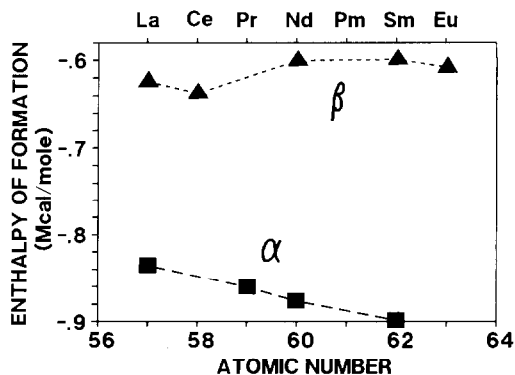


FIG. 4. The light rare-earth pyrosilicate enthalpies of formation calculated using the Born-Haber cycle are shown as a function of the atomic number ( $\alpha$ - $\text{RE}_2\text{Si}_2\text{O}_7$  = low temperature form,  $\beta$ - $\text{RE}_2\text{Si}_2\text{O}_7$  = high temperature form).

cause of the possible multiplying effects of upstream errors, this entropy calculation was only of academic interest and should be regarded appropriately.

## V. Conclusions

The simple summation of Coulomb energy predicted several simple crystal systems within 3 to 8% of the known lattice energies. The difference in the case of  $\alpha$ - $\text{Na}_2\text{Si}_2\text{O}_5$  was only 3%. The light rare-earth  $\alpha$ -pyrosilicate enthalpies of formation were calculated and ranged between -835 and -900 kcal/mole. Those of the high temperature polymorphs varied between -600 and -625 kcal/mole. It is anticipated that the actual values should be approximately 3% more negative.

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