

# **Reactions in Eucryptite-Based Lithium Aluminum Silicates**

Timothy Jochum and Ivar Reimanis<sup>†</sup>

Colorado Center for Advanced Ceramics, Metallurgical and Materials Engineering Department, Colorado School of Mines, Golden, Colorado 80401

The reaction sequence to synthesize  $\beta$ -eucryptite, LiAlSiO<sub>4</sub>, from the raw ingredients SiO<sub>2</sub>, Li<sub>2</sub>CO<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub> was studied using thermal analysis and X-ray diffraction techniques. Reactions were examined by heating the raw ingredients as twocomponent and three-component mixtures in air, then cooling for phase analysis. In some cases, cyclic heating was performed to ensure a complete reaction. It was found that a complex sequence of reactions involving several intermediate phases occurs. The single oxides (SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) react with Li<sub>2</sub>CO<sub>3</sub> to form the binary oxides (Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, Li<sub>2</sub>SiO<sub>3</sub>, and LiAlO<sub>2</sub>); SiO<sub>2</sub> reacts with Li<sub>2</sub>CO<sub>3</sub> before Al<sub>2</sub>O<sub>3</sub>. Subsequently, the binary oxides form ternary oxides form the equilibrium product,  $\beta$ -eucryptite (LiAlSiO<sub>4</sub>). These reactions are discussed in the context of the thermodynamic properties of the various compounds.

#### I. Introduction

β-EUCRYPTITE, LiAlSiO<sub>4</sub>, has interest in a variety of applications ranging from low coefficient of thermal expansion (CTE) materials to superionic conductors.<sup>1–3</sup> This material has a hexagonal crystal structure and belongs to the space group, *P*6<sub>4</sub>22. Polycrystalline β-eucryptite exhibits a slightly negative average CTE, resulting from the thermal anisotropy ( $\alpha_a = 8.6 \times 10^{-6}$ °C<sup>-1</sup>,  $\alpha_c = -18.4 \times 10^{-6}$  °C<sup>-1</sup>)<sup>4,5</sup> between the two main crystallographic directions of the hexagonal *a*-axis and *c*-axis. Composites with near-zero CTE may be designed by combining positive CTE materials with β-eucryptite. Aside from the unusual thermal properties, β-eucryptite also undergoes a pressureinduced phase transformation at ambient temperatures. The transformation has been observed by *in situ* synchrotron X-ray diffraction (XRD) as well as *in situ* Raman spectroscopy.<sup>6,7</sup> This unique behavior motivates fundamental studies to understand better the material structure–property relationships.

Processing of  $\beta$ -eucryptite and its composites is typically achieved by either a glass ceramic technique, whereby eucryptite crystals are formed within a glass matrix during ceramming,<sup>3</sup> or by powder synthesis and subsequent powder metallurgy.<sup>5,6</sup> In the latter case, control over stoichiometry, purity, and powder characteristics such as morphology, size, and size distribution is important as these factors will influence the sintering behavior as well as the final properties. Such a control may only be achieved if the sequence of reactions during the powder synthesis is understood. Previous studies<sup>5,6,8</sup> have shown that  $\beta$ -eucryptite forms when

Previous studies<sup>3,6,8</sup> have shown that  $\beta$ -eucryptite forms when the appropriate ratios of Li<sub>2</sub>CO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> are heated to about 1200°C according to the following reaction:

$$\mathrm{Li}_{2}\mathrm{CO}_{3} + \mathrm{Al}_{2}\mathrm{O}_{3} + 2\mathrm{SiO}_{2} \rightarrow 2\mathrm{Li}\mathrm{Al}\mathrm{SiO}_{4} + \mathrm{CO}_{2}(g) \tag{1}$$

The mechanism by which this reaction occurs has not been established. In air, the least stable of the three reactants in Reaction (1) is  $Li_2CO_3$ . Its decomposition in air is, as described by:

$$\text{Li}_2\text{CO}_3 \rightarrow \text{Li}_2\text{O} + \text{CO}_2(g)$$
 (2)

Reaction (2) is thermodynamically favorable when the concentration of CO<sub>2</sub> decreases below a critical value that depends on the temperature. For example, using the thermodynamic properties for the compounds in Reaction (2),<sup>9</sup> at 727°C, the critical partial pressure of CO<sub>2</sub> in air is about 0.13 torr.<sup>‡</sup> Our calculations with the program HSC Chemistry 5.1 (Outokumpo Research Oy, Pori, Finland) on the relative thermodynamic stability of Li<sub>2</sub>CO<sub>3</sub> in flowing air (~1 L/min) predict that decomposition begins to occur at about 600°C, well below the melting temperature of Li<sub>2</sub>CO<sub>3</sub> in the three-component mixture described in Reaction (1) decomposes at relatively low temperatures and produces Li<sub>2</sub>O, which is highly reactive with Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, as described in more detail below.

It is well established that  $Al_2O_3$  and  $SiO_2$  do not react with each other for the temperatures and times used to calcine  $\beta$ -eucryptite, <sup>11,12</sup> and thus the first reactions expected to occur involve Li<sub>2</sub>CO<sub>3</sub> or its decomposition product, Li<sub>2</sub>O. Previous research by Smirnov *et al.*<sup>13</sup> describes the physical behavior of Li<sub>2</sub>CO<sub>3</sub> with regard to the decomposition toward Li<sub>2</sub>O. The Li<sub>2</sub>CO<sub>3</sub>-Li<sub>2</sub>O system forms a eutectic at approximately 705°C and 13 mol% of Li<sub>2</sub>O. Thus, a reactive liquid is expected to form slightly below the Li<sub>2</sub>CO<sub>3</sub> melting point when the three reactants in Eq. (1) are heated. The formation of lithium aluminates and lithium silicates has been studied previously.<sup>14,15</sup> However, it is not well understood what sequence of reactions are present for the three-component mixture, as shown in Reaction (1).

The present study is motivated by the desire to determine and ultimately control the calcination process in the synthesis of  $\beta$ -eucryptite. The three different two-component raw mixtures comprising the reactants in Reaction (1) were prepared and characterized with thermal analysis and XRD, with the goal of better understanding how the two-component reactions may influence reactions in the three-component raw system.

## **II. Experimental Procedure**

### (1) Powder Preparation

Raw powders were mixed with a specific composition target of LiAlSiO<sub>4</sub>. As provided by Reaction (1), the ratio of Li<sub>2</sub>CO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> is [1:1:2], respectively. The mass ratio corresponding to this molar ratio is [1:1.38:1.63]. Lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>—Alfa Aesar, Ward Hill, MA), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>—CoorsTek, Golden, CO), and silicon oxide (SiO<sub>2</sub>—Sigma Aldrich, St. Louis, MO) were weighed and then mixed to achieve the ratio [1:1:2]. Because the Sigma Aldrich SiO<sub>2</sub> contains excess  $H_2O_3^{\$}$  the mass ratio used to weigh the powders

M. Rigaud-contributing editor

Manuscript No. 26940. Received October 9, 2009; approved December 14, 2009. This work was supported by the National Science Foundation Ceramics Program Grant #DMR-0746086 (TJ) and the U.S. Department of Energy's Office of Basic Energy Sciences Grant #DE-FG02-07ER46397 (IR).

<sup>&</sup>lt;sup>†</sup>Author to whom correspondence should be addressed. e-mail: reimanis@mines.edu

 $<sup>^{</sup>t}In$  ambient air in Golden, Colorado, where the present experiments were performed, this corresponds to about 200 parts per million (ppm) CO<sub>2</sub>. For comparison, the average CO<sub>2</sub> concentration in the Earth's atmosphere in 2009 is about 387 ppm (source: http://www.esrl.noaa.gov/gmd/ccgg/trends/).

<sup>&</sup>lt;sup>8</sup>It was determined in separate thermogravimetric experiments conducted by the authors that the Sigma Aldrich contains about 9% by mass  $H_2O$  which is bonded to SiO<sub>2</sub>; all of the excess  $H_2O$  leaves as a vapor when the specimen is heated to 400°C, and thus the  $H_2O$  is thought not to participate in any higher temperature reactions.

Material/mixture	Molar ratio
Li <sub>2</sub> CO <sub>3</sub>	Pure
$Al_2O_3$	Pure
SiO <sub>2</sub>	Pure (plus water)
$Li_2CO_3 - Al_2O_3$	[1:1]
$Li_2CO_3-SiO_2$	[1:2]
$Al_2O_3$ -SiO_2	[1:2]
Li <sub>2</sub> CO <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	[1:1:2]
Li <sub>2</sub> O–Al <sub>2</sub> O <sub>3</sub> –SiO <sub>2</sub>	[1:1:2]

 Table 1.
 List of Prepared Samples

was [1:1.38:1.85]. The particle sizes of the raw materials are:  $Li_2CO_3$ , ~1 µm;  $Al_2O_3$ , ~1 µm; and  $SiO_2$ , 50–70 µm. For the present study, two-component mixtures were studied to isolate specific reactions. Three two-component raw mixtures and one three-component raw mixture were prepared, approximately 30 g of each, as shown in Table I. One three-component raw mixture sample was prepared using lithium oxide ( $Li_2O$ —Alfa Aesar) rather than  $Li_2CO_3$ . Each powder mixture was blended by ball milling with aluminum oxide media for 24 h to ensure proper dispersion before analysis. Scanning electron microscopy with energy-dispersive spectroscopy was performed on the mixed powders to ensure intimate mixing.

# (2) Differential Scanning Calorimetry (DSC) and XRD Analysis

DSC was used to determine the initial energy profiles of each raw powder, two-component raw mixtures, and the three-component raw mixtures. A Netzsch STA 409C (Netzsch Instruments Inc., Burlington, MA) was used to gather DSC and thermogravimetric analysis (TGA) data concurrently. Highpurity aluminum oxide crucibles (purity level 99.7% Al<sub>2</sub>O<sub>3</sub>) obtained from Netzsch Instruments Inc. were used to contain the specimens. Platinum crucibles, also obtained from Netzsch Instruments Inc., were also used in some cases to confirm that the aluminum oxide crucibles did not contaminate the specimens. The heating profile for each run began at 20°C and was heated to 1200°C at 10°C/min. All experiments were performed in air that flowed through the apparatus at a rate of about 1 liter/minute. Because of the small specimen size required for the DSC, no soak at temperature is required. The raw mixtures were thermally cycled either twice or thrice to ensure a complete reaction during analysis.

Data gathered from the DSC instrument were used to generate a set of furnace treatments for each of the raw mixtures. The heat treatment procedure for each sample followed the same format. Furnace conditions consisted of a ramp rate of 5°C/min to the target temperature with a soak for 3 h followed by a furnace cool. Sufficient powder was used so that enough material was available for accurate XRD analysis (2–5 g). The XRD analysis was completed using a Philips X'Pert Pro Diffractometer (PANalytical Inc., Westborough, MA) with a copper source, with  $\lambda = 1.54$  Å, and a nickel filter. The detector used for all of the XRD analyses was an X'Celerator (PANalytical Inc.). The XRD data were characterized using both peak and profile data and a reference International Centre for Diffraction Data (ICDD) database.

#### III. Results

## (1) DSC Characterization

DSC of the raw powders is shown in Figs. 1 and 2. Both  $Al_2O_3$ and  $SiO_2$  are stable across the temperature range examined. The  $Al_2O_3$  exhibited no mass loss and the  $SiO_2$  exhibited a minor mass loss due to water. However,  $Li_2CO_3$  demonstrated a sharp melting peak and a set of peaks, which correspond to the loss of  $CO_2$ , consistent with previous studies.<sup>13</sup> The only raw material



Fig. 1. The differential scanning calorimetry/thermogravimetric analysis data from lithium carbonate exhibiting a sharp melting peak and a broad  $CO_2$  loss doublet, mass loss becomes significant just before the doublet at ~900°C.

that exhibited significant mass loss was Li<sub>2</sub>CO<sub>3</sub>. The DSC data from the two-component raw mixtures are shown in Figs. 3-5. The two-component raw mixtures that contained Li<sub>2</sub>CO<sub>3</sub> not only exhibited peaks corresponding to the melting of Li<sub>2</sub>CO<sub>3</sub>, but also showed subsequent chemical reactions. For example, Li<sub>2</sub>CO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> leads to three DSC peaks at approximately 800, 950, and 1100°C, and the Li<sub>2</sub>CO<sub>3</sub>-SiO<sub>2</sub> mixture exhibits endothermic peaks at approximately 1000° and 1050°C. The dashed lines on these diagrams indicate the temperatures from which specimens were cooled with the goal of performing XRD to establish the phases present. The DSC data from the two-component raw mixture of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> revealed no reaction up to 1200°C (Fig. 5). It is apparent from Figs. 3 and 4 that the mass loss in two-component raw mixtures containing Li<sub>2</sub>CO<sub>3</sub> occurs at a substantially lower temperature. For example, when Li<sub>2</sub>CO<sub>3</sub> is heated with Al<sub>2</sub>O<sub>3</sub>, the mass loss is significant at about 800°C, and when it is combined with SiO2, the mass loss occurs below 800°C. In contrast, Li<sub>2</sub>CO<sub>3</sub> alone exhibited significant mass loss at temperatures above 900°C.

DSC of the three-component mixture of raw materials exhibited multiple peaks, similar to the two-component raw mix-



Fig. 2. The differential scanning calorimetry data from  $Al_2O_3$  and  $SiO_2$  with no significant peaks. The thermogravimetric analysis data were omitted because a significant mass loss was not measured in either sample.



**Fig. 3.** The differential scanning calorimetry/thermogravimetric analysis data from the two-component mixture of  $\text{Li}_2\text{CO}_3$ :Al<sub>2</sub>O<sub>3</sub> showing the major reaction peak at ~740°C and the corresponding heat treatment temperatures of 780°, 850°, 1000°, and 1100°C.

tures, shown in Fig. 6. There are two main endothermic peaks; the first occurred at ~700°C and the second at ~1000°C. The three-component raw mixture that contained Li<sub>2</sub>O contained a similar endothermic peak at ~1000°C. However, the Li<sub>2</sub>O mixture revealed an exothermic peak at ~600°C in contrast to the endothermic peak observed in the Li<sub>2</sub>CO<sub>3</sub>-containing threecomponent mixture (Fig. 7). The mass loss for the Li<sub>2</sub>O mixture is negligible and attributed to the bonded water within the SiO<sub>2</sub> powder. The dashed lines in Fig. 6 pertain to the temperatures used to heat treat the powder mixture. Table II provides a comprehensive list of each temperature used for the heat treatment processes of the two-component mixtures. The three-component mixture heat treatments are described in Table III.

#### (2) XRD Characterization

XRD was performed on each specimen that was heat treated to the temperatures indicated by the dashed lines in Figs. 4–6, and these data are shown in Figs. 8–10. The diffraction data for the  $Li_2CO_3$ -Al<sub>2</sub>O<sub>3</sub> mixture confirmed the existence of the equimolar compound LiAlO<sub>2</sub> above 850°C. The heat treatments at 1000° and 1100°C show LiAlO<sub>2</sub> as a pure phase. The two-component mixture of Li<sub>2</sub>CO<sub>3</sub>-SiO<sub>2</sub> produced a mixture of two phases,



**Fig. 4.** The differential scanning calorimetry/thermogravimetric analysis data from the two-component mixture of  $\text{Li}_2\text{CO}_3$ :SiO<sub>2</sub> showing a major reaction peak at ~730°C and the corresponding heat treatments at 755°, 950°, 1010°, 1100°C. The significant peak at 1050°C was determined to be the melting of one of the species present.



Fig. 5. The differential scanning calorimetry data from the two-component mixture of  $Al_2O_3$ :SiO<sub>2</sub> with no reaction peaks. The thermogravimetric analysis data were omitted because they revealed only a minor mass loss due to water.

Li<sub>2</sub>SiO<sub>3</sub> and Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>. Before the first endothermic peak seen in the DSC, trace amounts of Li<sub>2</sub>SiO<sub>3</sub> were found in the heat treatment at 585°C. Based on differences in peak heights in Fig. 9, it is deduced that the heat treatment at 1100°C led to differences in the relative quantity of phases present from the heat treatments at 950° and 1010°C. However, the qualitative phase analysis is identical to the previous heat treatments. The difference in peak heights is likely due to the melt/solidification of the powder during this heat treatment, which may lead to preferential ordering of the material. The XRD data from the two-component mixture of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> after heat treatment (not shown here) revealed only two phases, which are identical to the starting constituents, consistent with published phase diagrams.<sup>11,12</sup> Included in Table II is the phase information gathered from the XRD analysis for each mixture. The twocomponent mixtures containing Li<sub>2</sub>CO<sub>3</sub>:SiO<sub>2</sub> and Li<sub>2</sub>CO<sub>3</sub>:Al<sub>2</sub>O<sub>3</sub> contained a small fraction of the raw materials, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> respectively, even after exposure to 1200°C and were excluded from Table III.

The XRD data gathered from each of the heat treatment temperatures for the Li<sub>2</sub>CO<sub>3</sub>-containing three-component

0.05 Li2CO3:Al2O3:SiO2 [1:1:2] 0.00 Heat Treatment Temperature 100 -0.05 Energy (uV/mg) -0.10 95 Vass (%) -0.15 90 -0.20 -0.2585 -0.30 -0.35 80 200 400 600 800 1000 1200 Temperature (°C)

**Fig. 6.** The differential scanning calorimetry/thermogravimetric analysis data from the three-component mixture of  $Li_2CO_3:Al_2O_3:SiO_2$  showing major reaction peaks at ~700° and ~1000°C. The corresponding heat treatment temperatures are shown here and listed in Table III.



**Fig. 7.** The differential scanning calorimetry/thermogravimetric analysis data from the three-component mixture of Li<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub> exhibiting an exothermic 600°C peak and an endothermic 1000°C peak and no significant mass loss.

mixture expose multiple compounds that appear and disappear during the calcination process. The major phases in the heat treatments at higher temperatures are the compounds containing all three cations (Li, Al, Si):  $\beta$ -spodumene (LiAlSi<sub>2</sub>O<sub>6</sub>) and  $\beta$ -eucryptite. Table III shows the transformation from raw materials to the existence of ternary oxide species, and ultimately pure LiAlSiO<sub>4</sub>.

## IV. Discussion

The experiments presented above reveal that a complex set of intermediate reactions occurs during the calcination described by Reaction (1). These are discussed next in the context of the thermodynamic properties of the various phases.

During heating, all mixtures containing Li2CO3 exhibit an endothermic peak at about 730°C, which corresponds to the melting of Li<sub>2</sub>CO<sub>3</sub>.<sup>10</sup> It is further evident that at about the same temperature (i.e.,  $\sim 730^{\circ}$ C), a chemical reaction occurs when Li<sub>2</sub>CO<sub>3</sub> is present. Based on the DSC data from the different two-component mixtures (Figs. 3 and 4), the product of the reaction that occurs at  $\sim 730^{\circ}$ C is either LiAlO<sub>2</sub> or Li<sub>2</sub>SiO<sub>3</sub>, depending on whether  $Li_2CO_3$  is present with  $Al_2O_3$  or  $SiO_2$ . XRD analysis of the heat treatments from the three-component mixtures shows that the reaction with SiO<sub>2</sub> occurs at a lower temperature. In fact, relatively small amounts of Li2SiO3 are even detected in the three-component mixture after a heat treatment of only 585°C. In this same temperature range where Li<sub>2</sub>CO<sub>3</sub> melts and chemically reacts, a significant mass loss is observed. The mass loss is likely due to the release of  $CO_2$ , which might occur by several mechanisms, as described below. In contrast, pure Li<sub>2</sub>CO<sub>3</sub> decomposes at a significantly higher temperature. Figure 11 reproduces the TGA data for pure Li<sub>2</sub>CO<sub>3</sub> and the various mixtures. In the light of these observations, the following are the possible reactions. The free energies of formation were calculated using HSC Chemistry 5.1 software at 700°C, and are indicated

$$\begin{array}{l} \text{Li}_2\text{CO}_3 + 2\text{SiO}_2 \rightarrow \text{Li}_2\text{Si}_2\text{O}_5 + \text{CO}_2(g) \\ \Delta G = -17.10 \, \text{kcal} \end{array} \tag{3}$$

$$\begin{array}{l} \text{Li}_2\text{CO}_3 + \text{SiO}_2 \rightarrow \text{Li}_2\text{SiO}_3 + \text{CO}_2(g) \\ \Delta G = -15.75 \text{ kcal} \end{array}$$

$$\tag{4} \label{eq:constraint}$$

$$Li_2CO_3 + Al_2O_3 \rightarrow 2LiAlO_2 + CO_2(g)$$
  

$$\Delta G = -11.13 \text{ kcal}$$
(5)

The following reactions are also considered in the context of Reaction (2), which has been reproduced again along with the

Table II.	Two Component	<b>Raw Mixture</b>	Heat Treatments
-----------	---------------	--------------------	-----------------

Mixture	Heat Treatment temperatures (°C)	Phases identified
$\begin{array}{c} Li_2CO_3 - Al_2O_3\\ Li_2CO_3 - SiO_2\\ Al_2O_3 - SiO_2 \end{array}$	780, 850, 1000, 1100 755, 950, 1010, 1100 None	LiAlO <sub>2</sub> Li <sub>2</sub> SiO <sub>3</sub> , Li <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>

calculated free energy of reaction at 700°C

 $\text{Li}_2\text{CO}_3 \rightarrow \text{Li}_2\text{O} + \text{CO}_2(g) \quad \Delta G = 18.07 \text{ kcal}$  (6)

$$\text{Li}_2\text{O} + 2\text{SiO}_2 \rightarrow \text{Li}_2\text{Si}_2\text{O}_5 \quad \Delta G = -35.16 \text{ kcal}$$
(7)

$$Li_2O + SiO_2 \rightarrow Li_2SiO_3 \quad \Delta G = -33.83 \text{ kcal}$$
 (8)

$$Li_2O + Al_2O_3 \rightarrow 2LiAlO_2 \quad \Delta G = -29.02 \text{ kcal}$$
 (9)

The decomposition of Li<sub>2</sub>CO<sub>3</sub> must result in the formation of a reactive lithium-containing species, which is likely Li<sub>2</sub>O (Reaction (2)). This decomposition to Li<sub>2</sub>O and CO<sub>2</sub> correlates with the specimen mass loss (shown in Figs. 1, 3, 4, and 6). Similarly, the reactions indicated by Reactions (2)-(5) are also accompanied by the loss of  $CO_2$  (g). By comparing the DSC data from the three-component raw mixture containing Li<sub>2</sub>CO<sub>3</sub> to the three-component raw mixture with Li<sub>2</sub>O, it is concluded that the endothermic reactions (Reactions (3)–(5)) are favored over the exothermic  $Li_2O$ -based reactions (Reactions (6)–(8)). However, the net free energy for the decomposition of Li<sub>2</sub>CO<sub>3</sub> (Reactions (2)) and the subsequent Li<sub>2</sub>O reactions (Reactions (6)–(8)) are very similar to the values for the direct  $Li_2CO_3$ reaction (Reactions (3)-(4)) making them indistinguishable experimentally. Despite the difference in mechanism between the two synthesis routes, both sets of reactions involve the release of  $CO_2$  (g) and produce identical intermediate compounds.

The intermediate species formed during the synthesis of  $\beta$ -eucryptite are not the only possible reaction products. Lithium aluminate species such as LiAl<sub>5</sub>O<sub>8</sub> and Li<sub>5</sub>AlO<sub>4</sub> are thermodynamically favored as well ( $\Delta G = -9.66$  and = -9.26 kcal, respectively). These species were not found during the XRD analysis and were thus eliminated as intermediate compounds. The absence of these products suggests that the lithium compounds (i.e. Li<sub>2</sub>CO<sub>3</sub> or Li<sub>2</sub>O) react with the SiO<sub>2</sub> completely before the reaction with alumina begins. It is recognized that local equilibrium conditions may vary, leading to the formation of compounds not thermodynamically predicted considering the overall composition.

In the present experiments, the aluminum-containing lithium silicates,  $\beta$ -spodumene (LiAlSi<sub>2</sub>O<sub>6</sub>), and  $\beta$ -eucryptite (LiAlSiO<sub>4</sub>), only formed above about 1000°C. Their formation corresponds to the second endothermic peak in the three-component raw mixture DSC data (~1000°C, Fig. 6).

 
 Table III.
 Heat Treatments—Li<sub>2</sub>CO<sub>3</sub> Three Component Raw Mixture

Temperature (°C)	Phases Detected
RT	$Li_2CO_3$ , $SiO_2$ , $Al_2O_3$
585	Li <sub>2</sub> CO <sub>3</sub> , SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , Li <sub>2</sub> SiO <sub>3</sub>
750	SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , Li <sub>2</sub> SiO <sub>3</sub> , LiAlO <sub>2</sub>
800	SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , Li <sub>2</sub> SiO <sub>3</sub> , LiAlO <sub>2</sub>
950	SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , Li <sub>2</sub> SiO <sub>3</sub> , Li <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> , LiAlO <sub>2</sub>
1050	SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , Li <sub>2</sub> SiO <sub>3</sub> , Li <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> , LiAlSi <sub>2</sub> O <sub>6</sub> ,
	LiAlSiO <sub>4</sub>
1100	SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , Li <sub>2</sub> SiO <sub>3</sub> , LiAlSi <sub>2</sub> O <sub>6</sub> , LiAlSiO <sub>4</sub>
1100 (15 h)	LiAlSiO <sub>4</sub>



**Fig. 8.** The comparison of  $\text{Li}_2\text{CO}_3:\text{Al}_2\text{O}_3$  heat treatment X-ray diffraction data showing the formation of only  $\text{LiAlO}_2(\bullet)$  at the expense of  $\text{Al}_2\text{O}_3(\bigcirc)$ .

The possible reactions to produce these include:

$$Li_2SiO_3 + SiO_2 + Al_2O_3 \rightarrow 2LiAlSiO_4$$

$$\Delta G = -14.87 \text{ kcal}$$
(10)

$$\text{Li}_2\text{Si}_2\text{O}_5 + \text{Al}_2\text{O}_3 \rightarrow 2\text{Li}\text{Al}\text{Si}\text{O}_4 \quad \Delta G = -12.85 \text{ kcal} \quad (11)$$

$$\begin{array}{l} \text{Li}_2\text{SiO}_3 + \text{Al}_2\text{O}_3 + 3\text{SiO}_2 \rightarrow 2\text{Li}\text{AlSi}_2\text{O}_6 \\ \Delta G = -12.14\,\text{kcal} \end{array}$$
 (12)

The product of Reaction (11) may react with the product of Reaction (8) to produce  $\beta$ -eucryptite according to the HSC calculations:

$$\begin{array}{l} \text{LiAlO}_2 + \text{LiAlSi}_2\text{O}_6 \rightarrow 2\text{LiAlSiO}_4 \\ \Delta G = -10.37\,\text{kcal} \end{array}$$
(13)



**Fig. 9.** The comparison of Li<sub>2</sub>CO<sub>3</sub>:SiO<sub>2</sub> heat treatment X-ray diffraction data, which shows the formation of the two lithium silicate phases. The phases are marked as follows: Li<sub>2</sub>SiO<sub>3</sub> ( $\blacklozenge$ ), Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> ( $\blacktriangledown$ ), and SiO<sub>2</sub> ( $\nabla$ ). The difference in appearance of the 1100°C scan is likely due to melting of the sample.



**Fig. 10.** The comparison of the three-component mixture, containing  $Li_2CO_3$ , heat treatment X-ray diffraction data, the onset of binary and ternary oxides are marked with  $\blacklozenge$  and  $\blacklozenge$ , respectively. The uppermost scan, labeled pure, is the result of a full calcination of this mixture.



Fig. 11. The comparison of thermogravimetric analysis data from  $Li_2CO_3$ -containing mixtures showing the earlier onset of mass loss corresponding to  $CO_2$  leaving the system. This illustrates the reaction between  $Li_2CO_3$  and  $SiO_2$  occurring at a lower temperature than the reaction between  $Li_2CO_3$  and  $Al_2O_3$ .

This *final* reaction is revealed in the DSC data between the 1050°C and the 1100°C heat treatments (Fig. 6). The progression of Reaction (12) was also confirmed by the XRD patterns of samples heat treated at these two temperatures (Fig. 9). The published and referenced procedure for synthesizing  $\beta$ -eucryptite by calcination calls for 15 h at 1100°C.<sup>5,6,8</sup> This soak time at 1100°C allows any nonequilibrium products to reach their equilibrium counterparts, and thus  $\beta$ -eucryptite as a pure phase.

#### V. Conclusion

The present study illuminates the reaction sequence for the calcination of Li<sub>2</sub>CO<sub>3</sub>, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> to produce  $\beta$ -eucryptite. By using DSC in combination with XRD, it is possible to draw the following conclusions. The reaction sequence for the given set of raw materials (Li<sub>2</sub>CO<sub>3</sub>, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>) is as follows: The single oxides (SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) react with Li<sub>2</sub>CO<sub>3</sub> to form the binary oxides (Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, Li<sub>2</sub>SiO<sub>3</sub>, and LiAlO<sub>2</sub>), SiO<sub>2</sub> reacts with Li<sub>2</sub>CO<sub>3</sub> before Al<sub>2</sub>O<sub>3</sub>. Subsequently, the binary oxides form ternary oxides (LiAlSi<sub>2</sub>O<sub>6</sub> and LiAlSiO<sub>4</sub>). Finally, the ternary oxides form the equilibrium product,  $\beta$ -eucryptite (LiAlSiO<sub>4</sub>).

#### Acknowledgment

The authors would also like to acknowledge the help of Michael Sanders for his expertise with the DSC and the resulting discussions, and Dr. Gerald Martins for helpful discussions.

#### References

<sup>1</sup>G. Orcel, J. Phalippou, and L. L. Hench, "Processing and Structural Evolution of (*x*Li<sub>2</sub>O · (1-*x*)Na<sub>2</sub>O) · Al<sub>2</sub>O<sub>3</sub> · 2SiO<sub>2</sub> Gels," *J. Non-Cryst. Solid*, **82**, 301–6 (1986).

<sup>2</sup>U. v. Alpen, H. Schulz, G. H. Talat, and H. Böhm, "One Dimensional Cooperative Li-Diffusion in β-Eucryptite," Solid State Commun., 23, 911-4 (1977). <sup>3</sup>W. Höland and G. Beall, Glass Ceramic Technology. the American Ceramic Society, Westerville, OH, 2002.

<sup>4</sup>W. W. Pillars and D. R. Peacor, "The Crystal Structure of Beta Eucryptite as a Function of Temperature," Am. Miner., 58, 681-90 (1973).

<sup>5</sup>A. I. Lichtenstein, R. O. Jones, H. Xu, and P. J. Heaney, "Anisotropic Thermal Expansion in the Silicate β-Eucryptite: A Neutron Diffraction and Density Functional Study," Phys. Rev. B, 58, 6219-23 (1998).

<sup>6</sup>J. Zhang, A. Celestian, J. B. Parise, H. Xu, and P. J. Heaney, "A New Polymorph of Eucryptite (LiAlSiO<sub>4</sub>),  $\varepsilon$ -Eucryptite, and Thermal Expansion of  $\alpha$ -and  $\varepsilon$ -Eucryptite at High Pressure," *Am. Miner.*, **87**, 566–71 (2002).

T. Jochum, I. E. Reimanis, M. J. Lance, and E. R. Fuller Jr., "In Situ Raman Indentation of  $\beta$ -Eucryptite: Characterization of the Pressure-Induced Phase

Transformation," *J. Am. Ceram. Soc.*, **92** [4] 857–63 (2009). <sup>8</sup>H. Xu, P. J. Heaney, D. M. Yates, R. B. Von Dreele, and M. A. Bourke, "Structural Mechanisms Underlying Near-Zero Thermal Expansion in  $\beta$ -Eucryptite: A Combined Synchrotron X-Ray and Neutron Rietveld Analysis," J. Mater. Res., 14, 3138-51 (1999).

<sup>9</sup>I. Barin and G. Platzki, Thermochemical Data of Pure Substances. Wiley and Sons Inc., Hoboken, NJ, 1997. <sup>10</sup>D. R. Lide (Ed.), CRC Handbook of Chemistry and Physics. CRC Press, Boca

Raton, FL, 2004. <sup>11</sup>J. F. MacDowell and G. H. Beall, "Immiscibility and Crystallization in

Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> Glasses," *J. Am. Ceram. Soc.*, **52** [1] 17–25 (1969). <sup>12</sup>R. F. Davis and J. A. Pask, "Diffusion and Reaction Studies in the System

Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>," *J. Am. Ceram. Soc.*, **55** [10] 525–31 (1972). <sup>13</sup>M. V. Smirnov, I. Ya. Lyubimtseva, L. A. Tsiovkina, and N. Yu., "Phase

Diagram of Lithium Carbonate-Lithium Oxide System," Krasnov, Zh. Neorg. Khim.-Russ. J. Inorg. Chem. (Engl. Transl.), 16 [1] 130-31 (1971).

<sup>14</sup>L. P. Cook, E. R. Plante, R. S. Roth, and J. W. Hastie. "Phase Equilibria of Stored Chemical Energy Reactants"; pp. 1–103. Annual Report to the Office of Naval Research for the Period May 25, 1983—May 25, 1984, Contract No. N00014-83-F-0117, Department of Navy, Office of Naval Research; Arlington, Virginia, 1984. <sup>15</sup>F. C. Kracek, "The Binary System Li<sub>2</sub>O–SiO<sub>2</sub>," *J. Phys. Chem.*, **34** [12] 2641–

50 (1930).