The High Temperature Chemical Reactivity of Li_2O

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ABSTRACT

The ultimate purpose of this study was to investigate the use of a Li-Ca mixture for direct reduction of actinide oxides to actinide metals at temperatures below 1500 °C. For such a process to be successful, the products of the reduction reaction, actinide metals, Li_2O, and CaO, must all be liquid at the reaction temperature so the resulting actinide metal can coalesce and be recovered as a monolith. Since the established melting temperature of Li_2O is in the range 1427 – 1700 °C and the melting temperature of CaO is 2654 °C, the Li_2O-CaO (lithium oxide-calcium oxide) pseudo-binary system was investigated in an attempt to identify the presence of low-melting eutectic compositions.

The results of our investigation indicate that there is no evidence of ternary Li-Ca-O phases or solutions melting below 1200 °C. In the 1200 - 1500 °C range utilizing MgO crucibles, there is some evidence for the formation of a ternary phase; however, it was not possible to determine the phase composition. The results of experiments performed with ZrO_2 crucibles in the same temperature range did not show the formation of the possible ternary phase seen in the earlier experiment involving MgO crucibles, so it was not possible to confirm the possibility that a ternary Li-Ca-O or Li-Mg-O phase was formed. It appears that the Li_2O-CaO materials reacted, to some extent, with all of the container materials, alumina (Al_2O_3), magnesia (MgO), zirconia (ZrO_2), and 95% Pt-5% Au; however, to clarify the situation additional experiments are required.

In addition to the primary purpose of this study, the results of this investigation led to the conclusions that:

- The melting temperature of Li_2O may be as low as 1250 °C, which is considerably lower than the previously published values in the range 1427 – 1700 °C.
- Lithium oxide (Li_2O) vaporizes congruently.
- Lithium carbonate and Li_2O react with 95% Pt-5% Au, and also reacts with pure Pt.
- It is likely that some or all of the past high temperature phase behavior and vaporization experiments involving $Li_2O(s)$ at temperatures above 1250 °C have actually involved $Li_2O(l)$. If these past measurements were actually measurements performed on $Li_2O(l)$ instead of the solid, the thermochemical data for phases and species in the Li-O system will require reevaluation.

1. INTRODUCTION

Pyrometallurgical processes employed for the production of actinide metals require a highly electropositive reductant. For, example, the traditional technique for Pu production has been fluoride “bomb reduction”, which involves heating Ca metal in a closed container with PuF_4 and PuO_2 to produce a Pu metal monolith and the Ca-containing slag. This is a high temperature process, requiring heating to about 550 °C to initiate the highly exothermic reaction that produces CaO, CaF_2 and Pu. The final temperature approaches 900 °C, which is sufficient to melt the CaO-CaF_2 eutectic, allowing the Pu metal to coalesce before solidifying. The rate of heating and the time at temperature are closely controlled to maximize metal conversion and minimize contaminants while producing an actinide monolith.

Alternative techniques, such as conversion of Cs_2PuCl_6 by Ca reduction, decomposition of PuH_{2+x}, and PuO_2 reduction by Li, have been investigated since the 1960s but these techniques result in the production of finely-divided Pu.[1] More recently, Li has been investigated as reductant in a molten salt process, employing a LiCl as a solvent, for the conversion of UO_2,[2] PuO_2,[2] and AmO_2[3] to the metallic state. This direct reduction process is achievable at a lower temperature, 650 °C, because the LiCl solvent has a normal melting point of about 610 °C.

The present work was undertaken to identify a reductant that can be utilized to reduce actinide oxides at temperatures below 1500 °C, producing a monolithic actinide product without involving halide salts. A mixed Li-Ca reductant is a likely candidate for this application due to the low melting temperatures of Li and Ca and the efficacy of these metals for reduction of actinides; however, such a reductant would be appropriate only if the products of the reduction process, CaO and Li_2O, form a solution that melts below 1500°C. Unfortunately, the phase behavior of the Li_2O-CaO system is largely uncharacterized and the system appears to have no published phase diagram. Furthermore, no stable ternary crystalline oxide phases including Li and any of the alkaline earth metals appear in standard thermochemical data tabulations[4,5,6] or in International Centre for Diffraction Data (ICDD) database.

It appears that this lack of data is related, at least in part, to the chemistry of Li-O system. Dilithium monoxide (hereafter referred to as lithium oxide or Li_2O), is one of five known oxide crystalline phases in this system; Li_3O_2, LiO, LiO_2, and Li_2O_2 have also been identified.[7] Lithium oxide may be formed by direct combination of Li and O_2 by heating Li(s) in the presence of excess O_2. This behavior is unique for the alkali metals, as the other metals react, under similar conditions, to form peroxides and superoxides.[8] In addition, Li_2O may be formed by the decomposition of Li_2CO_3.

Structurally, Li_2O is well characterized. It exhibits an anti-fluorite structure (similar to the face centered cubic (FCC) fluorite, CaF_2, structure except Li^+ cations reside in the fluoride positions and the O^{2-} anions reside in the calcium positions).[9] The high temperature behavior of this phase is not, however, as well understood as the structural behavior and the published information is somewhat inconsistent.

Chase et al.[10] evaluated the published data for this binary system (for the 1985 JANAF Table compilation), providing a thorough review of the literature through 1985. They reported that the most abundant vapor species over the pure solid are Li_2O, Li, and O_2, with lesser amounts of LiO and Li_2O_2; from their evaluation it appears that the phase Li_2O probably vaporizes congruently. Chase et al. chose a melting point of 1570 °C, but noted that published melting points for Li_2O were in the range 1427-1700 °C.[10] Chase et al. chose 2563 °C for the boiling point; however, for phases such as this one (which vaporize to form a variety of species, not just the "molecular species" that describes the stoichiometry of the condensed phase), the term boiling point has little meaning; this choice of boiling point is the temperature at which the fugacity of Li_2O reaches unity.[10]

The CRC Handbook[11] reports the melting point of Li_2O to be 1570 °C; the boiling point is not listed. The origins of the values in the CRC are not known (as no references are given for the values). The Outokumpu HSC Chemistry® for Windows thermochemical database tabulation[12] gives a melting point of 1570 °C and a boiling point of 2563 °C based on data from the 1993 thermochemical data tabulation of Barin et al.; these values are in agreement with the tabulations of Chase et al.

It should be noted that the published results upon which the thermochemical data estimations and phase behavior of the Li-O system are based are greater than 30 years old (and in some cases 50 or more years old). Based on the lack of recently published data, it appears this system is a candidate for further evaluation.

The Ca-O system is better understood than the Li-O system, especially on the Ca-CaO side of the binary phase diagram. Calcium oxide, with a melting temperature near 2654 °C,[13,14,15] is quite refractory. The phase diagram for this portion of the chemical system is well-characterized[14] and the thermochemical data for this system are well-established.[13,16] The structural characteristics of CaO are also well documented. Only one modification, which exhibits the halite FCC structure,[17] is stable at one atmosphere pressure.

The ultimate purpose of this experimental work was to investigate the Li2O-CaO pseudo-binary system for the presence of eutectic compositions. Based on the widely diverging melting temperatures of the two phases, 2654 °C for CaO and 1570 °C for Li_2O, it would be expected that any low-melting eutectic would be on the Li_2O-rich side of the phase diagram; however, because of the lack of knowledge about this chemical system, it seemed prudent to perform at least a cursory investigation that included compositions that ranged from about 90 mole percent (%) Li_2O:10% CaO to about 10% Li_2O:90% CaO (hereafter these mixtures will be referred to in shorthand notation: 90-10, 80-20, etc). Two techniques were implemented to elucidate the phase behavior of this system, (1)high temperature X-ray diffraction (XRD) experiments, during which the structural data were collected as the materials were heated up to temperatures of 1200 °C, and (2)heating samples in covered crucibles, under an ultrapure (99.99%) Ar(g) atmosphere, at temperatures up to 1500 °C, followed by structural studies of the quenched products of the heating experiments.

2. EXPERIMENTAL

2.1 Reagents

The reagents used during this study include lithium carbonate (Li_2CO_3) (Johnson Matthey, 99.999% metals basis, lot #S70393), calcium carbonate ($CaCO_3$) (Alfa Aesar, 99.99% metals basis, lot #22602), Li_2O (Alfa Aesar, 99.5% metals basis, lot #B23P38), and CaO (Alfa Aesar, 99.95% metals basis, lot #B14Q38).

Prior to use, the carbonates were dried in porcelain crucibles for about 1 hr at 105 °C in a Lindberg-Blue M 01430A-1 drying oven, removed hot, and allowed to cool to room temperature in a Nalgene desiccator charged with Drierite®. Based on the XRD analysis, the $CaCO_3$ dried at 105 °C was identified as monophasic calcite. A thermogravimetric analysis (TGA) of the Li_2CO_3 showed that it was contaminated with another phase, which decomposed at 400 °C. A subsequent high temperature XRD analysis of the material showed that lithium hydroxide (LiOH) appeared after the temperature was increased to a few hundred degrees Celsius. It is believed that this contaminant was due to the presence of Li_2O that reacted with water to form amorphous LiOH that was recrystallized when the sample was heated. Prior to use, the Li_2CO_3 was heated to 500 °C to decompose any LiOH present in the starting material. XRD analysis of this heated material identified the crystalline material as single-phase zabuyelite, Li_2CO_3. Also, the 50-50 and 80-20 Li_2O-CaO mixtures were analyzed by XRD prior to heating, and the only crystalline phases identified in these samples were Li_2O and CaO.

2.2 Crucible Materials

Four different crucible materials were utilized during this investigation: platinum-gold (95% Pt-5% Au), high-fired alumina (Al_2O_3), magnesia (MgO), and calcia-stabilized zirconia. Since the chemical composition of the Al_2O_3, MgO, and calcia-stabilized zirconia materials were not known, XRD data were collected on these materials. Diffraction patterns for the crucible materials showed:

- the Al_2O_3 crucible was nearly monophasic corundum, α-Al_2O_3, with a possible trace contamination of quartz;
- the MgO crucible was primarily periclase-MgO, with small amounts of two aluminum yttrium oxide phases, $AlYO_3$ and $Al_2Y_4O_9$ (believed to be residues remaining from the binder and/or grain stabilizing agents used for crucible manufacturing); and
- the calcia-stabilized zirconia was single-phase $Zr_{0.866}Ca_{0.134}O_{1.7}$.

2.3 Heating Experiments

Two types of heating experiments were performed - inert atmosphere furnace experiments and high temperature XRD experiments. The inert furnace experiments were conducted under ultrapure Ar(g) from 1300 to 1500 °C in a sealed CM Model 9000073 furnace equipped with molybdenum disilicide ($MoSi_2$) heating elements. Residual oxygen and water were removed from the Ar(g) using a Supelco titanium getter furnace. The exhaust from the furnace was bubbled through a solution of sodium hydroxide (NaOH) for the 1500 °C experiments and deionized water for the 1400 and 1300 °C experiments (to collect condensable species). Furnace temperature was controlled utilizing the vendor-supplied temperature control system installed on the furnace. To evaluate the accuracy of the temperature controller, the temperature reading of the furnace controller was compared to a standardized, type "S" thermocouple over the operating range of the furnace. This comparison showed that the systematic error of the furnace controller reading was less than ±10 °C over the entire range of the present study.

The ability of the metal oxides to undergo reactions with water vapor and carbon dioxide to form the hydroxides and carbonates, respectively (which have different melting temperatures than the oxides), made it necessary to handle these materials in an inert, dry atmosphere. Mixtures of Li_2O and CaO that ranged from 80% Li_2O to 80% CaO were produced by measuring appropriate masses of the two oxides on a calibrated Denver Instruments Model XS-310D balance and homogenizing the weighed samples with a clean agate mortar and pestle. These samples, in crucibles with lids, were placed in a desiccator before removal from the glovebox. The samples were quickly transferred from the desiccator to the furnace (which was being purged with ultrapure Ar) with a minimum of time in air.

The high temperature XRD experiments were performed on a Panalytical X'Pert Pro powder diffractometer with an Anton Paar HTK1200 (1200 °C maximum temperature) high temperature camera. The high temperature camera was operated under an ultrapure Ar(g) atmosphere. Samples were loaded on the sample cup in a dry, inert gas glovebox contained in a plastic vial and transferred to a desiccator while in the glovebox. The desiccator was subsequently transferred to the location of the diffractometer, where the sample mount was transferred to the high temperature camera. The camera, with atmospheric control capabilities (inert, reactive, or vacuum), was operated with an ultrapure Ar atmosphere, which was dried with an Altech Drierite® and molecular sieve columns. Upon completion of the diffraction experiment, the sample cup was transferred to the inert glovebox and new samples were loaded.

2.3.1.1 High Temperature Diffractometer Experiments

The 80-20, 50-50, and 20-80 Li_2O-CaO compositions were chosen for study by high temperature XRD. The first experiment, with the 50-50 mixture, was performed with the standard, high-temperature Al_2O_3 crucible. During this experiment the Li_2O attacked the Al_2O_3 sample stage (forming lithium aluminates), so subsequent experiments were performed with a 95% Pt-5% Au liner.

2.3.1.2 Metal Carbonate Inert Atmosphere Furnace Experiments

Inert atmosphere experiments were performed on two types of materials. The initial experiments were performed with carbonates; the later experiments were performed with oxides. The primary rationale for the use of carbonates was their ease of handling (the carbonates were handled on the open bench top). Appropriate masses of the dried carbonates were measured with a calibrated Mettler Toledo Model AB-204 balance and mixed in a clean agate mortar and pestle in an attempt to form homogenized mixtures. The mixtures had compositions varying at 10% intervals (so that after the carbonates decomposed, the mixtures would vary from 90-10 to 10-90 as the calcium and lithium oxides, respectively). A 2-g portion of each mixture was pressed into a 0.5” pellet (10 tons) using a Spex Model 3624B automated pellet press. The resulting pellets were placed in 95% Pt-5% Au crucibles in the inert atmosphere furnace and heated to 1300 °C. The carbonate pellets, with compositions corresponding to 10-90 to 90-10 Li_2O-CaO (after decomposition of the carbonates), were heated for 20 hours.

Based on the results of the first set of nine samples, a second set of nine samples was heated to 900 °C for about the same period of time as the first set.

2.3.1.3 Metal Oxide Inert Atmosphere Furnace Experiments

The remaining experiments, performed over the 1300-1500 °C range, were performed in the CM inert atmosphere box furnace because the temperature limit for high-temperature XRD furnace was 1200 °C.

1500 °C Experiments

Based on the earlier carbonate experiments that showed little reaction at 1300 °C, the next experiment was performed at 1500 °C in an attempt to see some reaction. Samples of the 80-20, 50-50, and 20-80 Li_2O-CaO compositions were contained in high-density, high-fired Al_2O_3 crucibles. A metallic block, with a mass many times greater than that of the crucibles and samples was fabricated with wells to contain the crucibles so that the crucibles could be cooled quickly upon removal from the furnace. The furnace temperature was increased from room temperature to 1500 °C at a rate of 6 °C per minute, the temperature was held at 1500 °C for an hour.

At the end of an hour, the furnace door was opened to allow removal of the crucibles. When the temperature of the furnace decreased enough to allow the operator to see the inside of the furnace, it was clear a reaction had occurred. The crucibles were barely visible, appearing to be embedded in the refractory baseplate of the furnace. Upon cooling the surface of the baseplate looked quite glassy. The off-gas bubbler was filled with an opaque, white vapor. A portion of one crucible was salvageable, and was removed from the furnace. The remainder of the materials from this experiment was not recoverable.

1400 °C Experiments

In this experiment, the 50-50 and 80-20 Li_2O-CaO mixtures were studied. The mixtures were contained in MgO crucibles (described earlier, primarily periclase) with Al_2O_3 lids. The furnace temperature was increased at 6 °C/minute from room temperature to 1413 °C. At 1413 °C, the furnace door was opened, and the crucibles were removed and placed on/in the cooling block. Within seconds, the temperature had fallen to below red heat, the lids were loosened, and the crucibles with loosened lids were placed in the desiccator and transferred to an inert gas glovebox for sampling. After the results of these experiments were reviewed, the 80-20 Li_2O-CaO mixture experiment was repeated in a $Zr_{0.866}Ca_{0.134}O_{1.7}$ (calcia-stabilized zirconia) crucible.

1300 °C Experiments

In this experiment, the 50-50 and 80-20 Li_2O-CaO mixtures were studied. The mixtures were contained in MgO crucibles (described earlier, primarily periclase) with Al_2O_3 lids. The furnace temperature was increased at 6 °C/minute from room temperature to 1300 °C. The temperature was held at 1300 °C for one hour, the furnace door was opened, and the crucibles were removed and placed on a large room temperature block to cool quickly. Within seconds, after the temperature had fallen to below red heat, an attempt was made to loosen the lids, but they were both stuck. The crucibles were placed in the desiccator and transferred to an inert gas glovebox where both crucibles were subsequently broken to retrieve their contents.

3. RESULTS and DISCUSSION

The experimental results can be logically partitioned into three sets: results that elucidate the sample-crucible interactions for the four crucible materials, results that elucidate the high temperature chemistry of mixtures of Li_2CO_3 and $CaCO_3$, and results that elucidate the high temperature chemistry of Li_2O and the reactivity of Li_2O and CaO. A summary of the high temperature heating experiments, which includes the experimental temperature, crucible material, sample composition, and a summary of the observed results, is presented in Table 1.

3.1 Crucible Materials

The choice of crucible materials was difficult due to the high temperature reactivity of the reagents, especially Li_2O. Four different crucible materials, 95% Pt-5% Au, Al_2O_3, MgO, and calcia-stabilized zirconia were studied.

3.1.1 95% Platinum-5% Gold

The initial choice, 95-5 Pt-Au, was made because it was believed that the 95% Pt-5% Au would be unreactive with the oxides and carbonates under consideration based on the results of Kudo et al.[18] who measured vapor pressures of Li_2O contained in Pt crucibles at temperatures up to 1700 K, and Takahashi and Watanabe[19] who decomposed Li_2CO_3 in Pt at temperatures below 1000 K. This belief proved to be erroneous. The residues from the present studies were very difficult to remove from the 95% Pt-5% Au containers, and the surface of the platinum was clearly altered by the interaction with the high temperature carbonate mixtures. Lithium platinates, Li_8PtO_6 and Li_2PtO_3, and elemental Pt were identified in recovered residues, indicating dissolution of the Pt by Li_2O. As the purpose of the Pt-Au alloy is to reduce the wetting of the Pt by glasses and cements, it appears likely that pure Pt would also undergo attack by both Li_2O and Li_2CO_3.

3.1.2 Alumina

Alumina crucible selection was made with the knowledge that a reaction of the Li_2O and crucible material (high density, high fired α-Al_2O_3) would probably occur; however, the melting temperature of the phase expected to be formed, $LiAlO_2$, is 1700 °C, [20] which is well above the maximum experimental temperature of 1500 °C. It was theorized that Li_2O-Al_2O_3 reaction would result in the removal of enough Li_2O from the sample to form lithium aluminum oxide ($LiAlO_2$) at the interface of the two materials, since the aluminate is stable up to 1700 °C. This material was only used for one experiment.

3.1.3 Magnesia

The impact of the minor phases $Al_2Y_4O_9$ and $AlYO_3$ is not known; however, after at least one of the experiments (1413 °C) there was a black residue visible on the outside of the MgO crucible. The XRD analysis of that material identified it as yttria (Y_2O_3).

No mention of Li-Mg-O phases was found during literature reviews; however, periclase-MgO melts at about 2850 °C,[21] which is slightly below 2925 °C, the melting point of CaO.[22] The similar chemistry of CaO and MgO suggests that if there is a eutectic in the Li_2O-CaO system there might be one in the Li_2O-MgO system as well, but possibly at an even lower temperature. The mass of Li_2O was kept much lower than the mass of MgO to decrease the likelihood that an unexpected reaction could result in a crucible breach. To check for sample-crucible interactions, used crucibles were sectioned and evaluated after the early experiments. The results of those analyses will be discussed later in the **RESULTS and DISCUSSION** sections associated with the specific experiments.

3.1.4 Calcia-Stabilized Zirconia

Calcia-stabilized zirconia crucibles were also utilized for these investigations. It was recognized that there was a likelihood that Li_2O would react with the crucible material; however, this material was utilized in an attempt to interpret the results from the experiments performed in MgO crucibles. Since the results from some of the experiments performed in MgO suggest that a new, unidentifiable phase was formed, the $Zr_{0.866}Ca_{0.134}O_{1.7}$ crucible was substituted for MgO, and the previous experiments were repeated.

3.2 Metal Carbonate Experiments

The carbonate experiments were designed to take advantage of the ease of handling of the carbonates, which physisorb small amounts of water, as compared to the oxides which react with water in the air to form hydroxides. Carbonates often lose carbon dioxide (CO_2) over a wide temperature range to form the metal oxides. Since it was known that Li_2CO_3 decomposes more readily than K_2CO_3 or Na_2CO_3,[23] it was expected that Li_2CO_3 and $CaCO_3$ could be decomposed to their respective oxides prior to melting or undergoing chemical reactions, leaving the oxides to react at higher temperatures.

The metal carbonate experiments were important because these experiments elucidated crucible-sample interactions with the 95% Pt-5% Au crucible material. The visual inspection of the sample material also provided qualitative information about reactivity. The Li-rich samples showed signs of melting, flowing, and resolidification. The samples with less than 50% Li_2CO_3

were expanded and distended. It was not possible to recover any material from the mixtures that flowed.

There was clearly reaction of the samples with the 95% Pt-5% Au crucibles. Platinum was the crucible of choice for Knudsen effusion vaporization studies of Li_2O[18] and for experiments to study the synthesis of Li_2O by the decomposition of Li_2CO_3.[19] While no reference to sample-crucible interactions were noted during those previous studies, it is clear that such interactions occurred during the present work.

3.3 Metal Oxide Experiments

Experiments were performed from room temperatures up to 1500 °C on Li_2O-CaO mixtures ranging from 90-10 to 10-90, respectively. The experiments at temperatures above 1200 °C provided the most significant results, with the results of the highest temperature experiment being the most interesting.

3.3.1 1200 °C Experiments

High temperature XRD analysis at temperatures up to 1200 °C did not show any changes in the reflections from Li_2O or CaO that could not explained by the expansion of the crystalline lattices due to the temperature increase. These experiments, while unremarkable, provide two important pieces of information. First, these experiments showed that there is no eutectic in the Li_2O-CaO system below 1200 °C. Second, along with the results of the 1300 °C experiments, these experiments were used to bound the melting point of Li_2O.

3.3.2 1300 °C Experiment

Experiments at this temperature were performed on two mixtures, 80-20 and 50-50 Li_2O-CaO mixtures. When the residues of these experiments were inspected, it appeared that at least a portion of both samples had melted. The heated samples were initially unconsolidated mixtures of granular solids.

After heating, the 80-20 sample was uniformly spread across the bottom of the crucible, solidifying to form a meniscus across the bottom of the MgO crucible and had a vitreous luster. The appearance of the 50-50 mixture was more interesting, with the sample appearing to be two unique phases, a sintered, crystalline-looking, nearly cylindrical mass of solid attached to a shallow solidified puddle of material (Figure 1). The XRD analysis of the puddle showed that it was primarily Li_2O with a small amount of CaO and MgO (Figure 2).

A possible explanation for the condition of the solid mixture is that MgO and/or CaO reacted with Li_2O, forming a pseudo-ternary (quaternary) solution (possibly a eutectic) with a melting point in the 1200-1300 °C range. As the liquid cooled, it re-crystallized into the three initial phases. While this explanation cannot be disregarded, it is unlikely for a number of reasons. First, in both sets of XRD data, the reflections for both Li_2O and CaO (and for that matter MgO) appear to be unshifted. If a solution had been formed, the quick cooling of the material upon removal from the furnace would be expected to retard the separation of the solution components into distinct phases. In the extreme case, cooling the liquid infinitely fast would be expected to result in an amorphous material. Slower cooling would be expected to produce either a new crystalline phase that incorporated all three cations into a single phase, or multiple mixed-metal phases in which more than a single cation type is present, and the resulting XRD data would reflect the presence of these substitutional cations. (There is an indication that this type of behavior occurred at 1413 °C. Those results were discussed below in the **1400 and 1413 °C Experiments** section).

The more likely explanation is that Li_2O melted and migrated, with assistance of gravity, to the bottom of the crucible where it formed a puddle. Upon cooling, it was stuck to both the crucible and the sintered (primarily CaO) portion of the sample. Due to the rough surface of the MgO crucible, some MgO from the sample-crucible interface was transferred to the sample when the sample was removed from the crucible. CaO was present as a granular material in the crucible and some CaO could have floated on or been suspended in the molten Li_2O, or could have been transferred from the sintered chunk when the sample was sectioned into two portions (the sintered mass and the thin layer).

It should be noted that a considerable quantity of Li_2O vaporized during this experiment. The lids were stuck on both crucibles (and the 80-20 crucible was damaged during lid removal) and the inside surface of both lids had a visible deposit of a whitish material. (Similar deposits were found on the inside of the crucible lid during the 1413 °C experiment).

3.3.3 1400 and 1413 °C Experiments

These experiments involved two crucible materials, MgO and calcia-stabilized zirconia ($Zr_{0.866}Ca_{0.134}O_{1.7}$). During the experiments with MgO crucibles, 80-20 and 50-50 Li_2O-CaO mixtures were studied, while for the $Zr_{0.866}Ca_{0.134}O_{1.7}$ experiments, only the 80-20 Li_2O-CaO mixture was studied.

The results of the 1400 °C 80-20 and 50-50 Li_2O-CaO mixtures contained in MgO were quite similar. Both samples appeared as puddles in the bottom of the crucibles upon recovery from the furnace, and the crucibles were destroyed while recovering the samples. The physical appearance of these samples suggested that Li_2O, CaO, and/or MgO may have reacted.

In addition to the material recovered from the crucible, the inside surface of each lid had a visible deposit (Figure 3) that consisted only of Li-bearing phases, $LiAlO_2$, formed from $Li_2O(g)$ and α-Al_2O_3, and Li_2CO_3 ,formed from $Li_2O(g)$ and $CO_2(g)$ (Figure 4). There was also a dark ring on the outer edge of the lid deposit and discoloration on the outside of the crucible as well (Figure 5). The XRD analysis of a portion of the black deposit from the outside of the crucible identified it as Y_2O_3, which was detected in the analysis of the crucibles before use and is commonly used in ceramic manufacturing as a grain boundary stabilizer.

While the analyses of the lid deposit and the Y-bearing residue on the outer surface of the crucible provide insights into the experiment, the most interesting result from this experiment was the solid recovered from the bottom of the crucibles. The XRD analysis of the product of the heated 50-50 mixture shows a d-spacing shift of the CaO reflections, which correspond to a decrease in the CaO lattice parameter from 4.809 Å to 4.799 Å, suggesting that there is incorporation of a foreign cation in the CaO structure (Figures 6 and 7). This result was not expected since it was assumed that the Li_2O, due to its lower melting temperature, would be the phase that would act as the solvent in the formation of a binary Li_2O-CaO phase.

The shift of the CaO reflections, and the reduction of unit cell parameter from 4.810 Å to 4.786 Å, was even more pronounced in the 80-20 product (Figures 8 and 9). In addition, the XRD data for the recovered product includes reflections near 23.5^o, 29.5^o, 35^o, and 46^o (in 2Θ) that are not assignable to either of the starting materials. Once again, the perturbation of the CaO reflections was observed, suggesting that a foreign cation has been incorporated into the structure, with magnesium the most likely choice.

The incorporation of magnesium is the most likely possibility since it is the most abundant. Both magnesium and calcium are alkaline earth metals, so it is possible their oxides might form a homogeneous single phase over a wide composition range. It could be argued that there should also be a Mg-rich phase with calcium present as the foreign cation; however, Mg^{2+} with a radius of 72 pm,[24] is much smaller than Ca^{2+}, with a radius of 100 pm,[24] so it is less likely that Ca^{2+} would be incorporated into MgO than Mg^{2+} into CaO.

The substitution of Li^{+} seems less likely. The substitution of the singly-charged Li^{+} for the doubly-charged Ca^{2+} at a Ca^{2+} position in the crystal lattice would result in a change in the net charge of the material unless other ions were substituted at interstitial locations. Furthermore, while a considerable amount of Li_2O was lost from the solid (based on the XRD reflection intensities from the before and after heating samples), it is supposed that most of this material was evaporated as large amounts of material were found on the underside of the crucible lids after each experiment.

It is possible that yttrium, which is present as a contaminant in the crucible material, has been incorporated into the CaO structure. This substitution seems unlikely because the amount of yttrium present is very small, and in no situation was yttrium detected in the samples from the inside of the crucibles. (The black Y-bearing phase was always found on the outside of the MgO crucible). Based on the available data, it appears that if a foreign cation is present in the CaO phase residing in the products of the 1413 °C experiments, that cation is most likely Mg^{2+}.

During this experiment, a whitish off-gas was again observed in the off-gas bubbler (as it had been observed during the 1500 °C experiment). After this experiment the solution was sampled. The inductively-coupled plasma-emission spectroscopy analysis of the bubbler solution showed the solution contained 18.4 mg/L molybdenum (Mo); it is believed that the molybdenum disilicide furnace elements were the source of the Mo.

After the 1413 °C experiments were completed, an additional experiment was performed at 1400 °C in an attempt to identify the origin of the unknown reflections in XRD data from the 80-20 1413 °C experiment. An 80-20 mixture was heated for 5 hours in an MgO crucible with an Al_2O_3 lid. The results from this experiment differed from the 1413 °C experiment (in which the sample was immediately removed from the furnace) in that there was no Li_2O remaining in the residue of the 5 hour experiment and the unidentifiable reflections were no longer present in the diffractogram; however, the unit cell parameter of CaO after heating was identical in both runs. These results indicate that the CaO phase is saturated with the foreign cation that is causing the lattice contraction.

In an attempt to determine the identity of the unknown crystalline phase(s) identified in the products from the experiments performed in the MgO crucibles, an 80-20 mixture was heated to 1400 °C in a $Zr_{0.866}Ca_{0.134}O_{1.7}$ crucible was performed. The product of this experiment was a whitish solid with the XRD pattern shown in Figure 10. Three phases were identifiable in the diffraction data: CaO; a reduced zirconium oxide, Zr_3O_{1-x}; and lithium zirconium oxide, $Li_{1.82}ZrO_3$. In addition, numerous unidentifiable reflections were also present near 23.5^o, 29.5^o, 35^o, and 46^o in 2Θ (as had been the case with the residue from the 80/20 material heated in an MgO crucible).

3.3.4 1500 °C Experiment

This experiment provided the most interesting results. The temperature of this experiment, 1500 °C, was chosen based on the accepted melting point of Li_2O, 1570 °C. Since the expected product of an Al_2O_3-Li_2O reaction, $LiAlO_2$, melts at 1700 °C or greater,[10] it was assumed that the sample-crucible interactions would result in the removal of only enough Li_2O

from the sample to form the ternary phase at the interface of the two materials, as the experimental temperature, 1500 °C, is actually below the accepted melting point of Li_2O, 1570 °C.[10] Instead, the experiment resulted in fusing of the crucibles to the furnace refractory, formation of a liquid that consumed much of the furnace lining and the Al_2O_3 crucibles, and transport of an opaque whitish vapor from the furnace to the off-gas system. Based on the analyses of the residues from this experiment, it appears that the furnace lining, which is a composite material containing cristobalite (melting point 1723 °C),[25] mullite (melting point 1850 °C),[26] and α- Al_2O_3, and the Al_2O_3 crucible reacted with the contents of the crucible.

When this experiment was performed, the results were somewhat perplexing; however, with the aid of the results of later experiments that show the melting temperature of Li_2O is in the range 1200-1300 °C, it is hypothesized that the Li_2O melted, dissolved the bottom of the α-Al_2O_3 crucible, and subsequently reacted with the furnace refractory to form liquid Li-Al-Si-O phases, such as spodumene,[27] eucryptite,[28] and petalite[29], all of which are molten or decompose below 1500 °C. Supporting this hypothesis is an analysis of the recovered refractory which shows that pseudoeucryptite ($Li_{0.9}AlSiO_4$) was present in the cooled residue, along with Al_2O_3, $LiAl_5O_8$, $Al_6Si_2O_{13}$, and $Ca_{0.88}Ä_{0.12}Al_{1.77}Si_{2.23}O_8$ (Figure 11).

3.4 Relationship of the Present Results to Past Investigations

The present investigation was initiated as a study of the melting point of Li_2O and CaO mixtures. During this investigation it was observed that a 50% Li_2O-50% CaO mixture appeared to have separated into two phases, a CaO phase that appeared sintered, and a phase that appeared to have melted that was found to be predominantly Li_2O, suggesting that the melting point of Li_2O may be less than 1300 °C. This temperature regime is much lower than the previously published melting points of Li_2O, which range from 1427-1700 °C, with 1570 °C being chosen as the accepted melting point by Chase et al.[10]

In an effort to understand the wide discrepancy between the present result and the previously published results, while recognizing that the materials studied in the present experiments are less pure than the materials studied in some earlier investigations, the results of the past three decades were perused to identify studies during which the residues from the heating experiments were characterized. In the study of Takahashi and Watanabe,[19] micrographs of the solids recovered from heating experiments (during which Li_2O was contained in Pt) at 1100 °C, 1150 °C, 1200 °C, 1250 °C, 1300 °C, and 1350 °C were presented. While these black and white images are somewhat difficult to interpret, the images from the three highest temperatures look markedly different than the two lower temperature images. The images from the two highest temperature residues (1300 and 1350 °C) show surfaces that are essentially devoid of topographic features, suggesting that these materials are probably solid condensates from previously melted material. In addition, the 1250 °C image shows very large grains with little fine structure, suggesting that this material may also have experienced a liquid to solid phase transition during cooling.

The study of Ortman and Larsen[30] addressed the synthesis, characterization, and melting point determination Li_2O. The melting point determination gave a melting point of 1438 °C, which is at the low end of the range of values discussed by Chase et al.[10] This temperature is considerably higher than the melting temperature indicated by our work, 1200 - 1300 °C, and the melting point indicated by the results of Takahashi and Watanabe,[19] whose micrographs indicate that melting probably occurred as low as 1250 °C. Based on the description of the experimental method, in which cooling curves were generated (and the melting temperature was taken as the portion of the curve at which m = 0), while the temperature was being measured via an optical pyrometer, it is plausible that the temperature was not accurately measured. It seems possible that two sources of error could contribute to the discrepancy between the present measurements and those of Ortman and Larsen. One possible source of error at these low temperatures could be that the surface emissivity of the sample varied as the experiment proceeded. A second (and related uncertainty) possibility is that the length to diameter ratio of the "cavity" being viewed was too low, leading to unreliable temperature measurement. In any event, this large discrepancy between the "accepted" melting temperature and our recent results (which appear to be corroborated by the results of Takahashi and Watanabe)[19] suggests the phase behavior and the chemistry of the Li-O system should be reevaluated to ensure the thermodynamic data for this system are consistent with actual chemical behavior of the system since earlier experiments performed at temperatures above 1250 °C were most likely performed on liquids and not solids.

In addition, it appears that the choice of Pt as a crucible material for high temperature studies involving Li_2O may not have been appropriate. The purity of the Pt used in the earlier studies[18,19,30] is unknown. For the present work, 95% Pt-5% Au crucibles were utilized in an attempt to inhibit the wetting of the crucibles by the molten Li_2O; however, the chemical composition of the Pt utilized during previous investigations[18,19,30] is unknown. The results of the present study, and of an earlier study during which Pt was detected in Li_2O residues recovered from samples melted in Pt,[30] show that the reactivity of Pt and Li_2O may have been underestimated during two earlier studies.[18,19]

4. CONCLUSIONS

The primary purpose of the present experimental work was to evaluate the utility of a Li-Ca reductant for the reduction of actinide oxides to metals. Since the product of such a reduction would include Li_2O and CaO, it was necessary to investigate the formation of a pseudo-binary solution in the Li_2O-CaO system. The experimental results from the present study were not definitive with regard to the presence of intermediate phases or a low-melting solution or eutectic in the Li_2O-CaO system. There is experimental evidence that Li_2O may form a solution phase through reaction with CaO and/or MgO; however, to further elucidate the phase behavior of this system, more study is required. There is also an indication that Li_2O may melt at or below 1300 °C; this apparent low melting point of Li_2O suggests that it might be possible to reduce actinide oxides to metal, at temperatures as low as 1300 °C under an inert gas atmosphere, utilizing a Li-rich mixture of Li and Ca if the resulting CaO displays adequate solubility in Li_2O.

In addition to the primary purpose of this study, other worthwhile information related the high temperature chemistry of the Li-O system, specifically the melting point of Li_2O and the reactivity of Li_2O and Li_2CO_3. Based on the results of the present investigation and results from a previous investigation,[19] it is concluded that the melting temperature of Li_2O is could be as low as 1250 °C, as opposed to the literature values in the range 1427 – 1700 °C.[10] During the present study, experiments at 1200 °C, which involved mixtures of Li_2O and CaO, gave no indication that any portion of any mixture had melted; however, at 1300 °C a puddle of material that X-ray diffraction analysis showed to be primarily Li_2O,, with lesser amounts of LiOH, MgO and CaO, was found at the bottom of the MgO crucible that had originally contained a 50-50 Li_2O-CaO mixture. This observation is also supported by the results of Takahashi and Watanabe[19], whose micrographs suggest that the melting point of Li_2O may be as low as 1200 – 1250 °C. This lower melting temperature for Li_2O is a partial explanation for the high reactivity of the Li_2O with the high-fired α-alumina crucible during our 1500 °C heating experiments.

Our present results suggest Li_2O vaporizes congruently, which is in agreement with the evaluation of Chase et al. This conclusion is based on two observations. First, during numerous experiments in which the crucibles containing Li_2O-CaO mixtures were covered during heating, condensate was found on the inside of the crucible lid. The condensate was identified as Li_2CO_3, the phase that would expect to be present if Li_2O had reacted with $CO_2(g)$ in the atmosphere (the samples were processed on the bench top subsequent to the heating experiments), and $LiAlO_2$, an expected reaction product when Al_2O_3 and Li_2O interact at high temperatures. Second, during the 1300 °C experiments a puddle of Li_2O was found at the bottom of the MgO crucible (it had melted and separated itself from the sintered material present in the crucible). If Li_2O did not vaporize congruently, it would be expected that Li-bearing phases other than Li_2O would be identified.

Our results also show that Li_2CO_3 and Li_2O react with 95% Pt-5% Au crucibles. Published results of high temperature experiments in which Li_2CO_3 and Li_2O were contained in Pt (of unknown purity) made little[30] or no mention[18,19] of reactivity of samples and containers.

Lastly, it is very likely that the past high temperature phase behavior and vaporization experiments involving $Li_2O(s)$, at temperatures above 1250 °C probably involved $Li_2O(l)$. If the melting temperature of Li_2O is actually at or below 1250 °C, the thermodynamic quantities for condensed Li-O phases and Li-O vapor species may be in error. Treatment of experimental measurements to determine thermodynamic quantities requires identification of the phases on which the measurements are being made. If measurements in the temperature range 1250-1570 °C were actually measurements performed on $Li_2O(l)$ instead of the solid, the thermochemical data for phases and species in the Li-O system will require reevaluation. This issue could be significant because the standard Gibbs free energy of reaction for the reduction of UO_2 by Li at 1327 °C,

UO_2(s, 1327 °C) + 4 Li(s, 1327 °C) = 2 Li_2O(l, 1327 °C) + U(l, 1327 °C),

is +9.2 kcal.[6] If the free energy of formation of Li_2O(l) were 5 kcal more negative, this reduction reaction, and the reduction reactions of Li(l) with crystalline NpO_2, PuO_2, and AmO_2, would be thermodynamically spontaneous at 1327 **°C**, possibly eliminating the need for the presence of Ca for the reduction of actinide oxides to metals.

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FIGURES

Figure 1. 50-50 Li_2O-CaO mixture after heating at 1300 °C for 1 hour.

Figure 2. XRD pattern of white crust on the bottom of the 50/50 mole% mixture of Li_2O and CaO after heating for 1 hour at 1300 °C. The presence of $LiOH{\cdot}H_2O$ is most likely an artifact of material handling outside the dry glovebox.

Figure 3. Deposits on the inside surface of crucible lids from 1413 °C experiment. The deposits appear to be whitish on the inside surface of the face of the lid with a dark ring around the periphery. The location of the dark ring corresponds to the outside edge of the crucible lip.

Figure 4. XRD pattern of d**eposit scraped from the underside of the lid of the 1413 °C experiment. The presence of the carbonate, instead of the oxide, is indicative of air exposure during sample handling.**

Figure 5. Dark deposit on the outer surface of MgO crucible used for 1413 °C experiment.

Figure 6. XRD pattern of the **50-50 Li_2O-CaO mixture after heating to 1413 °C.**

Figure 7. Comparison of selected reflections for the starting material (50-50 mixture) and the product from the 1413 °C experiment. The black trace (the far left hand peak and the

more intense peak near 33.62 °) is from the unheated material, while and the red trace (the second peak from the left and the les intense peak near 33.62 °) is from the heated material.

Figure 8. Comparison of the before heating and after heating 2Θ values and intensities for selected reflections from the 80-20 material. The black trace (the far left hand peak and the more intense peak near 33.6 °) is from the unheated material, while and the red trace (the second peak from the left and the less intense peak near 33.6 °) is from the heated material.

Figure 9. Comparison of the before heating and after heating 2Θ values and intensities for selected reflection from the 80-20 material after 5 hours at 1400 °C. The black trace is from the unheated material and the red trace is from the heated material.

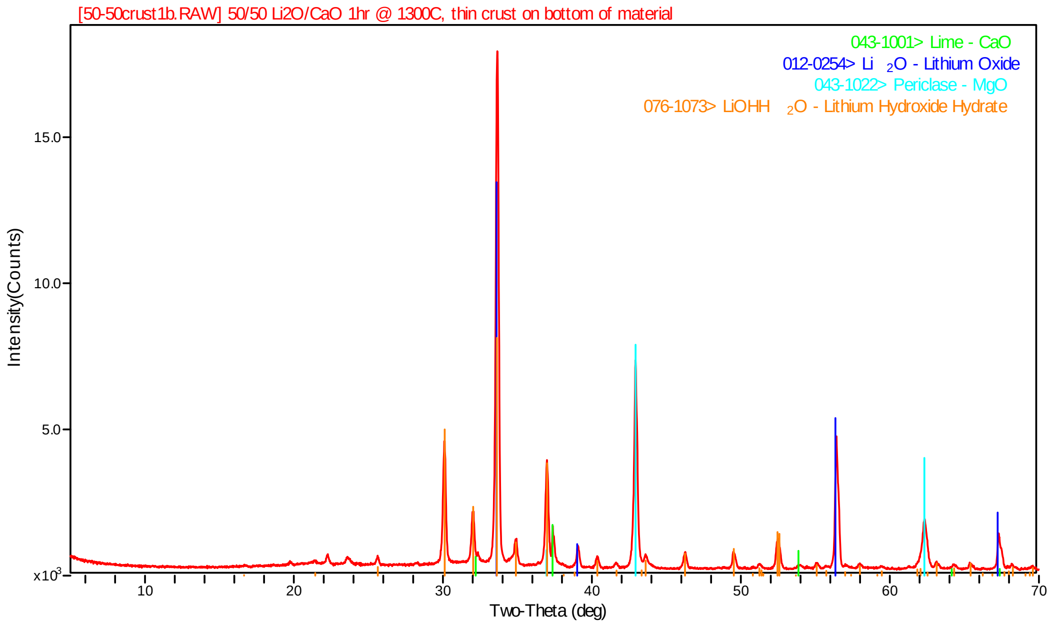
Figure 10. XRD pattern of the **80 mole% Li_2O: 20 mole% CaO heated for 1 hr at 1400 °C in a $Zr_{0.866}Ca_{0.134}O_{1.7}$ crucible. Numerous unidentified reflections are present in the diffraction pattern.**

Figure 11. XRD pattern **of a sample of recovered furnace refractory after the 1500 °C experiment.**

Tables

Table 1. Compilation of experimental results from Li_2O-CaO heating experiments.

Figure 1. 50-50 Li_2O-CaO mixture after heating at 1300 °C for 1 hour.



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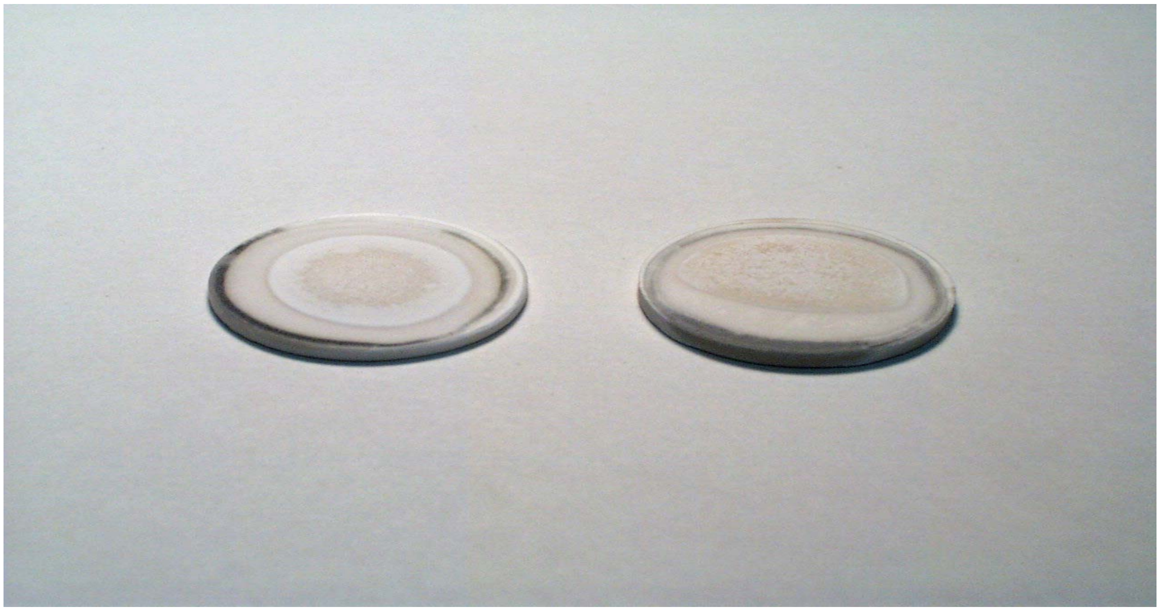

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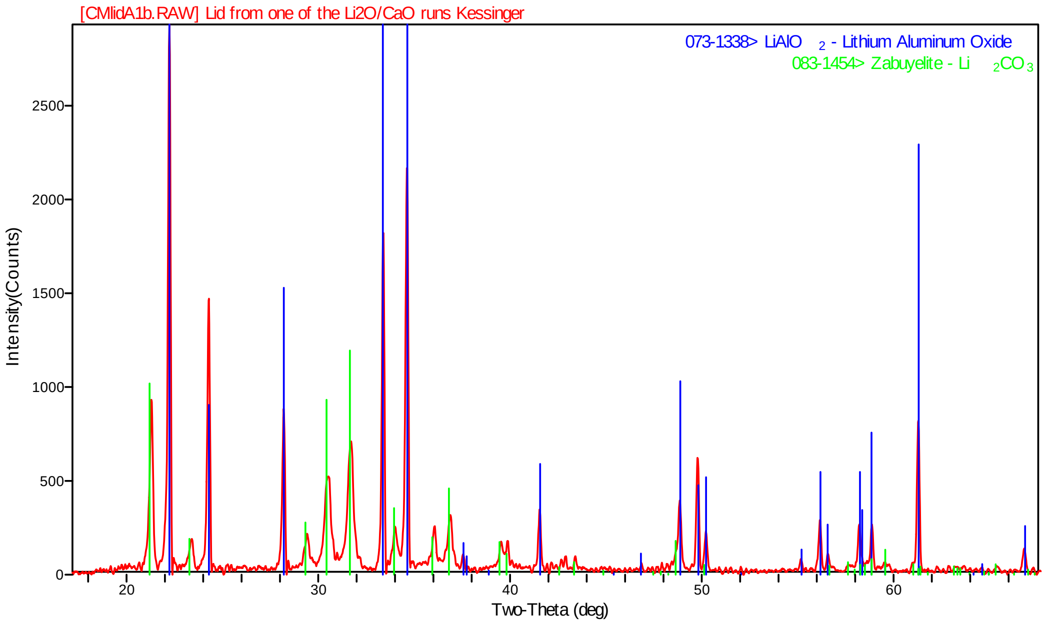

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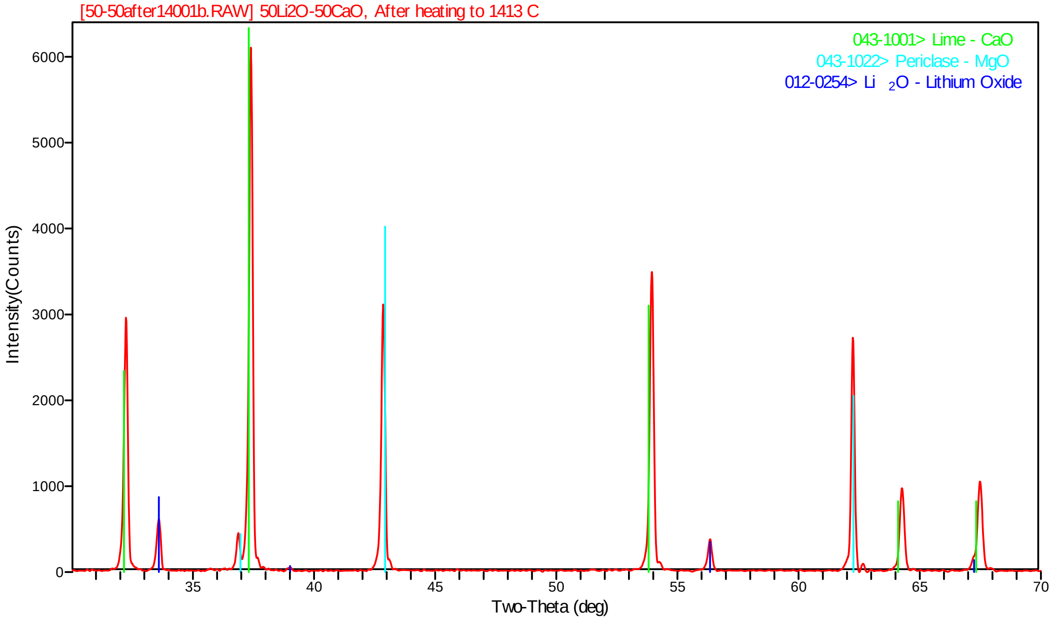
Figure 5. Dark deposit on the outer surface of MgO crucible used for 1413 °C experiment.



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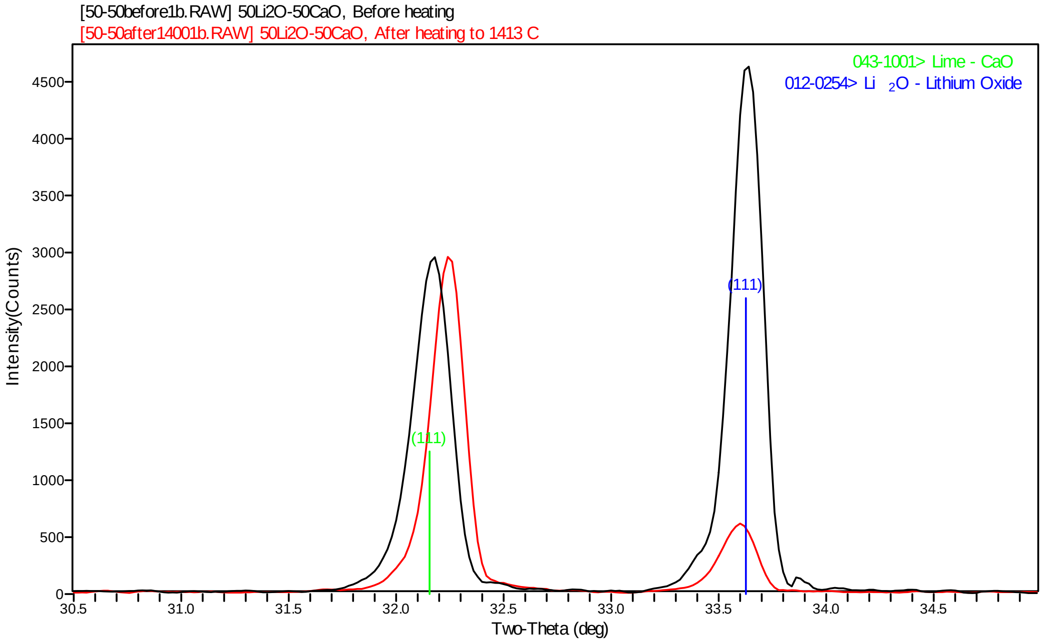

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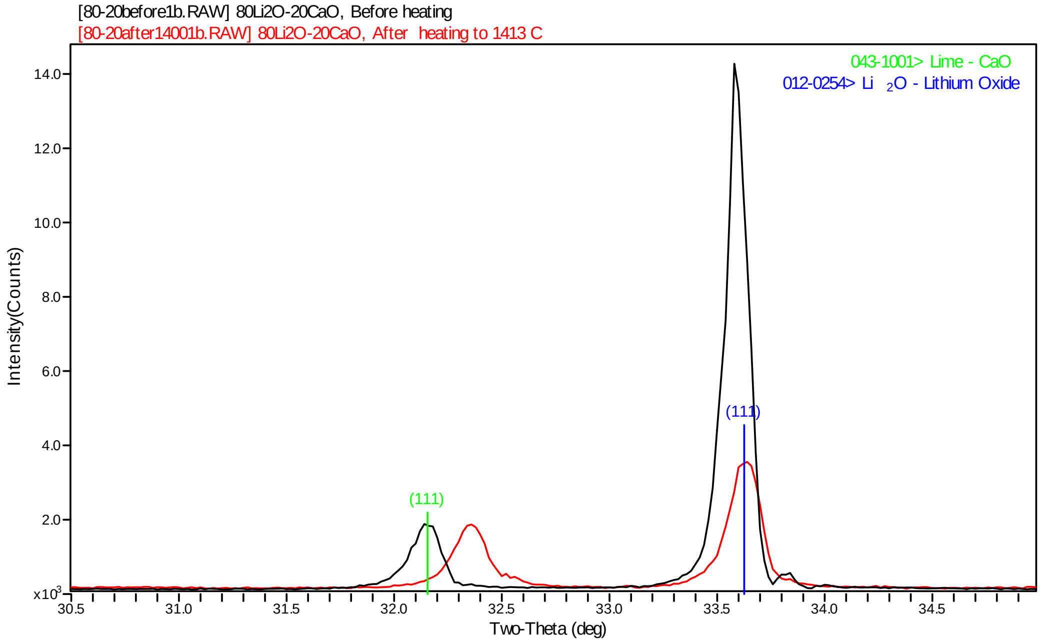

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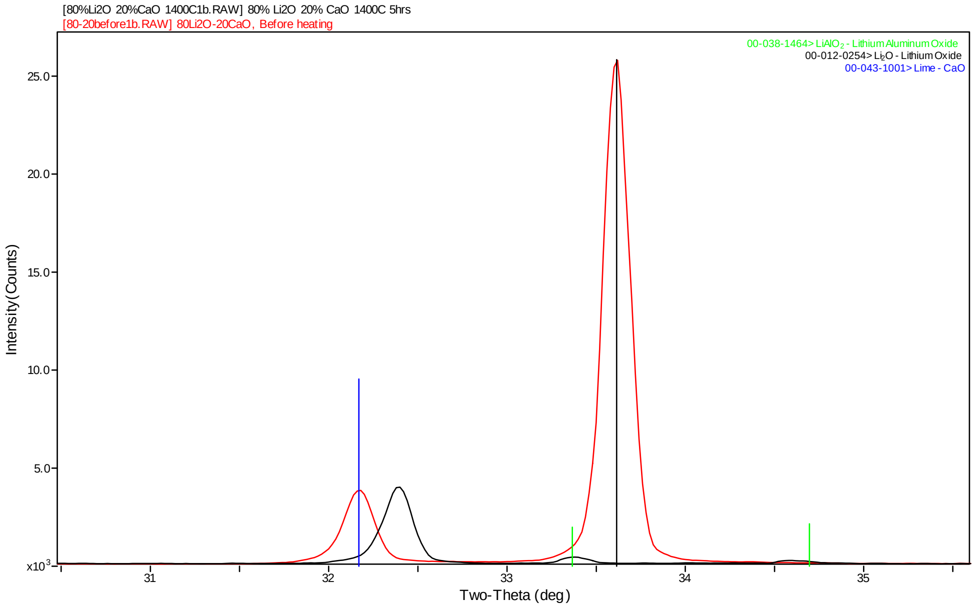

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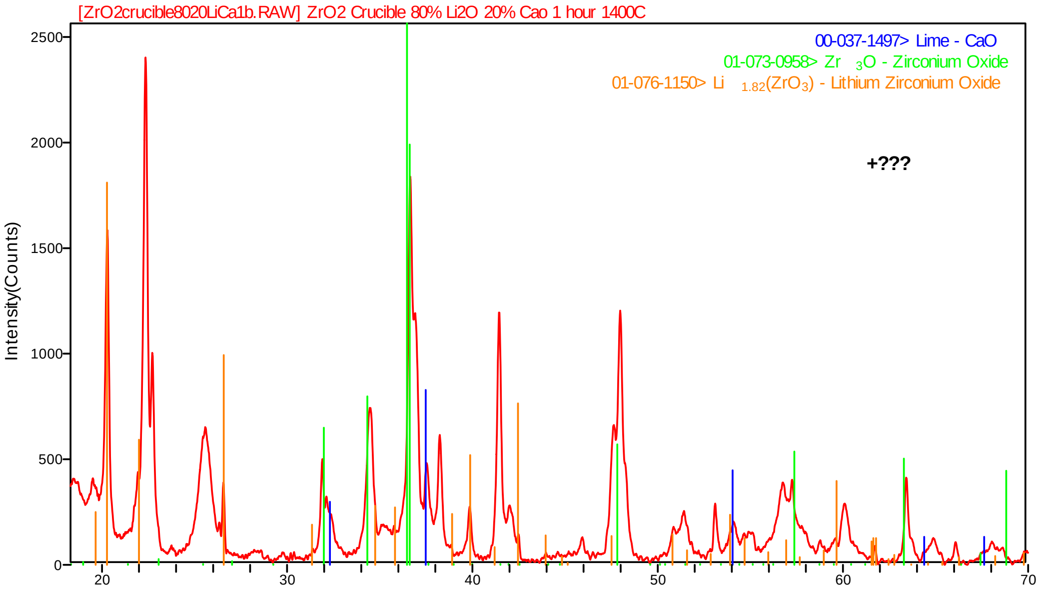

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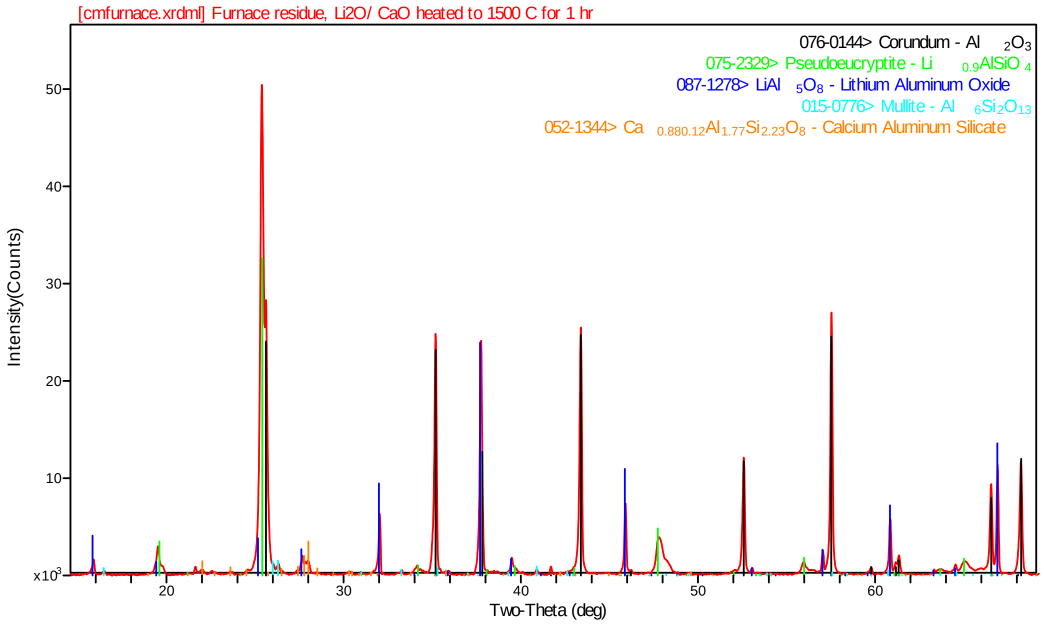

Figure 11. XRD pattern of a sample of recovered furnace refractory after the 1500 °C experiment.

T/°C	Crucible	Sample Composition	Comments
1200	Al_2O_3	80%Li_2O-20%CaO 50%Li_2O-50%CaO 20%Li_2O-80%CaO	XRD experiments performed as temperature ramped from ambient to 1200 °C samples reacted with crucible to form aluminates, CaO and Li_2O present in residue no melting observed
1300	MgO	50%Li_2O-50%CaO	at temperature for 1 hour cylindrical sample separated - Li_2O appeared to have melted, CaO sintered
1300	MgO	80%Li_2O-20%CaO	at temperature for 1 hour extensive melting of sample
1300	95%Pt-%5Au	10%Li_2O-90%CaO to 90%Li_2O-10%CaO (as carbonates)	cylindrical samples at temperature for 20 hours samples with 50% or more Li_2O showed signs of melting samples with less than 50% distended longitudinally all samples exhibited extensive reaction with crucible no sample residues recovered
1400	MgO	80%Li_2O-20%CaO	5 hours at temperature residue contained CaO and an unknown phase, CaO d-spacing shifted no Li_2O detected in sample residue
1400	$Zr_{0.866}Ca_{0.134}O_{1.7}$	80%Li_2O-20%CaO	residue contained CaO, Zr_3O_{1-x} and $Li_{1.82}ZrO_3$ and an unknown phase
1413	MgO	80%Li_2O-20%CaO	sample temperature ramped up from ambient to 1413 °C, then quenched residue contained CaO and an unknown phase, CaO d-spacing shifted $LiAlO_2$ and Li_2CO_3 detected on inside of crucible lid Y_2O_3 deposits on outside of crucible
1413	MgO	50%Li_2O-50%CaO	Sample temperature ramped up from ambient to 1413 °C, then quenched residue contained CaO and an unknown phase, CaO d-spacing shifted $LiAlO_2$ and Li_2CO_3 detected on inside of crucible lid Y_2O_3 deposits on outside of crucible
1500	Al_2O_3	80%Li_2O-20%CaO 50%Li_2O-50%CaO 20%Li_2O-80%CaO	all samples melted all samples reacted with furnace refractory $Li_{0.9}AlSiO_4$, Al_2O_3, $LiAl_5O_8$, $Al_6Si_2O_{13}$, and $Ca_{0.88}\ddot{A}_{0.12}Al_{1.77}Si_{2.23}O_8$ present in residue recovered from furnace

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