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The Preparation, Characterization and Melting
Point of Lithium Oxide, II. The Preparation and
Melting Point of Octalithium Zirconate**

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**August 1982
(revised March 1983)**

UWFDM-449

***FUSION TECHNOLOGY INSTITUTE
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STUDIES ON TRITIUM BREEDERS FOR FUSION REACTORS

- I. The Preparation, Characterization and Melting Point of Lithium Oxide
- II. The Preparation and Melting Point of Octalithium Zirconate

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UWFD-449

*This work was initiated under a contract with the Electric Power Research
Institute and the Fusion Engineering Program of the University of Wisconsin-
Madison.

THE PREPARATION, CHARACTERIZATION AND MELTING POINT
OF HIGH PURITY LITHIUM OXIDE

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ABSTRACT

High purity lithium oxide was synthesized by thermal decomposition of the peroxide at temperatures up to 1070 K under dynamic vacuum. Analyses of typical preparations gave carbonate 0.01-0.02%, hydroxide 0.0-0.2%, sodium 0.002%, manganese 0.0004%, and lithium oxide 99.8-100.0%. The corrected melting point was measured as 1711 ± 5 K based on the thermal arrest observed when molten specimens were cooled.

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I. Introduction

Lithium oxide is an attractive candidate as a tritium breeder in a fusion reactor because of its high lithium atom density. One other criterion for an acceptable solid breeder is a high melting point. In the case of lithium oxide considerable uncertainty exists about the value of the melting point as evidenced by the assorted values, 1700 K,¹ 1843 K,^{2,3} 1898 K,⁴ 1973 K,^{5,6} > 1973 K,^{7,8} 2000 K⁹ tabulated in the reference and review literature.

The original papers from which the melting point data were obtained, do not allow one to select the best value with a high degree of confidence. Jaeger and van Klooster,¹⁰ in 1914, in conjunction with a phase study on the lithium oxide-silicon dioxide system, were unable to melt lithium oxide despite heating to 1898 K and concluded that the melting point was probably "in the neighborhood of 1700°C" (1973 K). Unfortunately this observation has been widely referenced.⁴⁻⁸ Van Arkel,¹¹ in a study (1953) on the electrical conductivity of a number of molten oxides found lithium oxide to melt quite sharply at 1843 K. This is cited^{2,3} in two well used sources of thermodynamic data, yet it must be suspect because the magnesium oxide crucible used was strongly attacked by the molten lithium oxide. Brewer and Margrave¹² (1955), in a study on the vapor pressure of lithium and sodium oxides, observed the melting point with an optical pyrometer and estimated it to be "in the range of 1700±15 K." More recent determinations strengthen support for a melting point in the vicinity of 1700 K. In a study of the lithium oxide-lithium carbonate phase diagram, Papin¹³ (1969) found the melting point to be 1705±5 K, and Akiyama¹⁴ (1980) in the investigation on the synthesis of single crystals of lithium oxide, determined the melting point to be 1703±2 K.

Unfortunately, in the experiments cited, very little attention was paid to the purity of the lithium oxide. Either no analyses were performed^{10,11,14} or the composition was established by titration^{12,13} alone. Since a titration with standard acid measures the total base present, i.e. oxide, hydroxide and carbonate, the calculated purity will be high unless an independent determination of either carbonate or hydroxide is made. The purity reported by Akiyama¹⁴ is a spectrographic analysis for metal content and does not provide any information on the hydroxide and carbonate content of the product, which according to the manufacturer may be as high as ten percent.¹⁵

In addition to all these uncertainties, confusion about the melting point apparently has been compounded by instances in which the temperature was tabulated as °C¹⁶ when in fact the original data were reported in degrees Kelvin.¹² The work reported here seeks to resolve these issues by determining the melting point using a well-designed experimental approach on carefully prepared well-characterized samples of lithium oxide.

II. Experimental

(1) Preparation of Lithium Oxide

Lithium oxide was synthesized in ~ 70 g batches by thermal decomposition of lithium peroxide under vacuum. The peroxide, in turn, was prepared using a modification of the technique of Bach and Boardman.¹⁷ In the procedure used here all transfers and manipulations were done in an inert atmosphere. Approximately 225 g of lithium hydroxide monohydrate (Sargent Welch) was placed in a one liter polyethylene bottle along with 0.2 liters of 30% hydrogen peroxide. Mixing was achieved by vigorous shaking of the capped bottle for twenty minutes. To separate excess lithium hydroxide from the product, 0.50 liters of methanol were added and the mixture shaken for another twenty

minutes. The peroxide product was filtered, washed three times on the funnel with 50 mL of methanol and dried in an inert atmosphere.

The yellow peroxide was transferred to an appropriately sized Pyrex tube (50 mm x 260 mm) and the remaining methanol removed by pumping on the vessel for 2-3 days at room temperature. The thermal decomposition of the peroxide to the oxide was initiated by heating the Pyrex vessel at 570 K under reduced pressure for 2-3 days until the pressure dropped to ~ 1 Pa. The white, powdered product was then transferred to a (304) stainless steel vessel of approximately the same volume as the Pyrex vessel and heated incrementally from 570 K to 1070 K under vacuum over a period of 2-10 days. Each time the pressure in the vessel dropped to about 1 Pa, the temperature was raised to the next step. Lithium oxide synthesized by this technique had a purity of > 99.8 wt%. Two separate batches of lithium oxide prepared in the above manner were used in the melting point experiments.

(2) Analytical Methods

The total base content of lithium oxide samples was determined by titration with standard 0.6 M hydrochloric acid using a Leads and Northrup expanded scale pH meter and Orion combination pH electrode. Lithium oxide samples were loaded into flip top cap polyethylene vials in an inert atmosphere, sealed, and weighed externally. Empty vials were handled in exactly the same way and at the same time.

The carbonate content was determined by a modification of the procedure described by Pobiner.¹⁸ In this analysis, carbon dioxide released upon acidification of a carbonate-containing sample is collected in an IR gas cell and the peak height of the 2360 cm^{-1} carbon dioxide band is compared to an empirically determined standard curve of peak height versus carbonate concentration.

The detailed procedure follows. Samples (~ 300 mg) were loaded into pre-weighed gelatin capsules and isolated from the atmosphere by placing them in polyethylene vials. Blanks were run to establish the reproducibility of the handling and weighing technique and to determine corrections necessary for the adsorption or desorption of water on the capsule. The filled gelatin capsule was removed from the vial and dropped into a 3-necked 150 cc round bottom flask containing 25 mL of 6 M hydrochloric acid. The flask, which was attached to the gas handling system, had been purged with nitrogen before adding the sample. The dissolution of the capsule and sample was accelerated by stirring. The carbon dioxide accumulated was collected in an evacuated infrared gas cell and the spectrum obtained on a Digilab FTS-20 Fourier Transform Infrared Spectrometer.

Metal ion impurities in the lithium oxide preparations were determined by neutron activation analysis. Weighed samples (~ 0.5 g) contained in flip top cap polyethylene vials were irradiated in the University of Wisconsin Nuclear Reactor at a neutron flux of 4.1×10^{12} n/cm²-s (pneumatic tube irradiation) for 120 s and then counted for 300 s periods at 0.33, 6.46 and 26.9 hours after completion of irradiation. Identification of specific elements was made by measuring the intensity and energy of peaks in the gamma ray spectrum of a sample using a multichannel analyzer and Tracer Northern TN-11 on-line computer. Quantitative analysis of the elements present was made by comparison with standards prepared with coal fly ash supplied by the National Bureau of Standards. After 37 days some of these samples were re-irradiated at a neutron flux of 1.1×10^{13} n/cm²-s (whale tube irradiation) for 720 s and counted at 2.47, 24.2, and 266 hours after completion of irradiation. This higher fluence irradiation was performed to check for the presence of chromi-

um, nickel and iron in the samples. Blanks were also run on empty polyethylene vials at low fluence pneumatic tube and high fluence whale tube irradiations.

(3) Other Instrumental Procedures

Samples were examined for the presence of phases other than lithium oxide by powder patterns. These were obtained with a Phillips x-ray unit using nickel filtered copper K α radiation. The patterns were recorded on film mounted in a 114.57 mm Debye-Scherrer camera. Exposures of 7 to 20 hours were used for samples packed in 0.3 mm Lindemann glass capillaries. The d values obtained were compared with those for known compounds using the powder diffraction file published by the JCPDS International Centre for Diffraction Data (Swathmore, PA, USA).

Visible spectra of colored lithium oxide crystals were obtained between 300 and 600 nm on a Cary 17D spectrometer. Samples were prepared in the dry box as Nujol mulls on filter paper and run in air (~ 10 minutes) with the reference channel containing Nujol on filter paper.

Lithium oxide samples were examined for evidence of sintering using a JEOL JSM-35C scanning electron microscope (SEM) with beam energy of 25 keV and magnifications ranging from 150 to 2000. Samples were affixed to an aluminum rod with silver paint adhesive and coated with either chromium or aluminum (Model HUS-4GB Hitachi Evaporator) to provide good electrical conductivity. No etching or polishing of samples was performed.

(4) Melting Point Apparatus and Procedure

The melting point apparatus consisted of a graphite resistance furnace (Astro Industries, Inc., Santa Barbara, CA, Ultra High Temperature Furnace, Model No. 2570C), crucible, cover with aperture, mirror and an optical pyro-

meter (Pyrometer Instrument Co., Inc.). A flowing argon atmosphere was maintained in the furnace when in operation.

The only modification made in the furnace was the introduction of a 2-piece cylindrical graphite shield which served as a protective barrier between the heating elements and the crucible containing the molten sample. The crucible was thermally isolated from the floor of the graphite shield by a thin sheet of molybdenum metal and a layer of graphite felt. The crucibles used were either platinum (30-50 cm³) or tungsten (80 cm³). The covers were either molybdenum (2.6 mm aperture) or graphite (2.8 mm aperture). The crucibles were filled roughly one-half to three-quarters full of sample, with the void volume above the sample providing the blackbody.

Melting point measurements were performed as follows. The sample was heated until molten, the power to the furnace was then turned down and the sample allowed to cool. One observer followed the brightness of the cavity aperture with the optical pyrometer while a second recorded the time. Time versus temperature plots were then constructed after temperature corrections were made for non-unity emissivity of the cavity and the reflectivity of the mirror. To verify the performance characteristics of the equipment, the melting points of aluminum oxide and lithium fluoride were determined. The line of best fit through the plateau points was determined by least square analysis of the data. The temperature at the mid-point of the plateau was designated as the melting point.

III. Results and Discussion

(1) Preparation of Lithium Oxide

Research workers studying the properties of lithium oxide have generally prepared their own samples by one of three routes, namely: thermal decompo-

sition of the hydroxide,¹⁹⁻²¹ carbonate,^{12,22-26} or the peroxide.^{17,27-33} We did not use the hydroxide because of the very reactive nature of the vapor phase species, nor the carbonate because of the difficulty in decomposing the last traces of carbonate.²⁵ The peroxide provided a relatively low temperature route to the oxide and, with appropriate precautions in handling, a high purity product. For example, it is very important to wash the precipitated peroxide with methanol to remove the last traces of any unreacted hydroxide, and equally important to remove residual methanol by pumping on the peroxide at room temperature. Failure to carry out these procedures effectively results in products which sinter at low temperature and which are substantially contaminated with corrosion products from the metal vessel used in the final thermal decomposition step.

The highest quality products were obtained by decomposing, in vacuo, the peroxide in a Pyrex vessel at a relatively low temperature (< 600 K) until the pressure dropped to < 1 Pa. Under these conditions the peroxide was substantially decomposed and the product was still free-flowing. However, to achieve complete decomposition within a reasonable time, this product then was heated, in vacuo, in a stainless steel vessel. The temperature was raised in stages each time the pressure dropped to < 1 Pa with a maximum temperature of about 1100 K reached over a period of two days. Scanning electron micrographs showed that sintering of the particles had started at this temperature. The products used for the melting point experiments were selected from the white center of the sintered reaction product core and analyzed to be 99.8-100 percent Li_2O (Table I). Occasionally the lithium oxide had a bluish tinge to it which disappeared upon further heating. Optical absorption spectra of these products showed a band between 560 and 570 nm, a shoulder in the 400-410 nm

TABLE I. ANALYSIS OF Li_2O SAMPLES (wt%)

<u>Sample</u>	<u>Mole Base^a/100 g</u>	<u>Li_2CO_3</u>	<u>LiOH</u>	<u>Li_2O</u>	<u>Metals x 10²</u>
A					
Initial	6.695±0.005	0.01±0.01	0.00	100.0	0.2 Na, 0.04 Mn
Fused ^b	6.683±0.008	0.06±0.01	0.20	99.7	0.1 Na, 0.02 Mn, 3 Pt
Fused ^b	6.682±0.009	0.20±0.02	0.04	99.7	0.1 Na, 0.4 Mn, 4 Pt
B					
Initial	6.688±0.011	0.02±0.01	0.20	99.8	0.2 Na, 0.02 Mn
Fused ^b	6.678±0.006	0.05±0.01	0.40	99.5	0.1 Na, 0.02 Mn, 4 Pt
Fused ^b	6.672±0.018	0.10±0.03	0.70	99.2	0.06 Na, 0.08 Mn, 2 Pt
Fused ^c	6.589±0.017	0	---	~ 98	0.05 Na, 0.1 Mn, 70 W

^aMoles of base/100 g Li_2O (100%) is 6.694

^bPt crucible

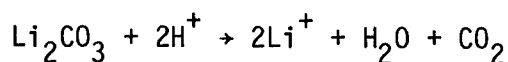
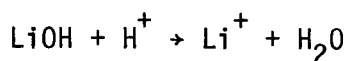
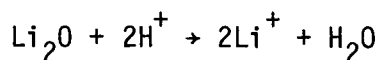
^cTungsten crucible

region and a very strong absorption at ~ 320 nm. These spectra are similar to those for the blue products obtained by neutron irradiation of lithium oxide, suggesting that F centers have been produced during the decomposition of the peroxide. The traces of manganese found are evidence that contamination from the walls of the reaction vessel was not completely eliminated. In fact, if oxidation of the metal vessel sidewalls is not minimized, x-ray evidence for Li_5FeO_4 and LiCrO_2 is found in the oxide in contact with the metal sidewalls.

(2) Analyses and Sample Purity

(a) Analyses. Neutron activation analyses of lithium oxide preparations show that the metal impurity concentrations are low (Table I). The 10^{-3} wt% of sodium must originate in the lithium reagent, and the 10^{-4} wt% manganese must come from the metal reaction vessel used in the high temperature thermal decomposition step. The concentrations of iron, zinc, cobalt and chromium, as determined by neutron activation analysis, are essentially indistinguishable from the concentrations of these elements found in the polyethylene vials used to contain the lithium oxide. No independent analyses for these elements were made, on the assumption that the low metal impurity content would not affect the melting point determination.

The absence of a significant concentration of metal impurities allows us to equate the total number of moles of protons used in the titration of a lithium oxide sample with standard acid, to the total number of moles of lithium in the sample.



The titration data, along with the sample weight and an independent determination of carbonate, allows the calculation of the hydroxide content and thus the complete description of the sample composition.

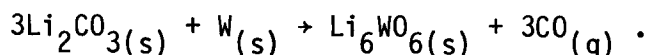
The titrations were run in triplicate. The standard deviation for each set of samples was typically 1.5 parts per thousand (ppt), which is high compared to standard deviation of less than 1 ppt for the standardization of the acid with tris(hydroxymethyl)aminoethane. The lower precision is due to the handling procedure which introduced an error of ± 0.10 mg in the weight of lithium oxide. Since the sample size was ~ 300 mg the uncertainty in the sample weight was about 0.3 ppt.

The gelatin capsules used as sample container for the carbonate analysis were observed to lose about 3 ± 0.3 mg during the course of the loading procedure. This amounted to an uncertainty of about 1 ppt in the sample weight. The limit of detectability for carbonate was $\sim 0.01\%$ and the precision of the determination, as indicated by triplicate analyses of many samples was about $\pm 0.01\%$ for levels of carbonate < 0.20 wt%. However, the gas handling procedure itself introduces an error which probably is greater than the error in the weighing procedure.

(b) Sample Purity. The products obtained here (Table I) via the peroxide route are of better quality than most previously reported. G.K. Johnson,²⁵ who prepared the oxide from the carbonate, reported a final purity of 99.67% Li_2O , with 0.18% carbonate, 0.1% sodium and smaller amounts of other metallic impurities. Although not calculated, the hydroxide content must have been low since the titration data agreed well with the rest of the analytical data. Aarons,²⁶ who also prepared the oxide from the carbonate, reported the presence of $\sim 2.3\%$ hydroxide and assumed that the carbonate was all decom-

posed. H.L. Johnston and Bauer,¹⁹ who prepared the oxide by thermal decomposition of the hydroxide, corrected their titration data for the presence of calcium and reported the purity as 99.74% Li₂O and 0.26% calcium oxide. However, lithium hydroxide and carbonate were assumed to be absent in this case. Anno,³³ who also prepared the oxide from the hydroxide, reported a purity of 98.1% Li₂O with the remainder being hydroxide. Kudo³⁴ determined carbonate and hydroxide but did not titrate for total base. The lithium oxide they used had a purity of only 91.5%.

It is to be noted (Table I) that the carbonate and hydroxide concentrations of the fused product are higher than observed in the original preparations. This contamination undoubtedly occurs in the handling of the samples and illustrates the extreme sensitivity of lithium oxide to water vapor and carbon dioxide. It is interesting to note that no carbonate is found in samples fused in a tungsten crucible. This can be explained by the reaction



X-ray powder patterns of samples fused in tungsten clearly show the presence of Li₆WO₆. As a result of this reaction or a similar one with the hydroxide, tungsten proved to be a poor container material. Small concentrations of platinum are always found in products fused in platinum containers. Other qualitative observations suggest that the presence of platinum is also related to reactions with lithium hydroxide and/or carbonate rather than with lithium oxide. These observations point out the fact that it is difficult to avoid contamination of lithium oxide with hydroxide and carbonate even when handling

and transfers are made in what normally would be considered an inert atmosphere.

(3) Melting Point Measurements

The emissivity of the blackbody was estimated by Bedford's³⁵ and Gouffe's³⁶ equations. Bedford's equation is

$$\epsilon_a = 1 - \frac{(1 - \epsilon)}{\epsilon} \frac{\Omega}{2\pi} \quad (1)$$

and Gouffe's equation is

$$\epsilon_a = \epsilon'_a (1 + k)$$

where

$$\epsilon'_a = \frac{\epsilon}{\epsilon[1 - (S/s)] + (S/s)} \quad (2)$$

and

$$k = (1 - \epsilon)[(s/S) - (\Omega/2\pi)] .$$

In these equations, ϵ_a = the effective emissivity of the cavity aperture, ϵ = the spectral emissivity of the cavity inner wall, Ω = the solid angle of radiation emerging from the cavity aperture having its apex at the intersection of the viewing axis with the back wall of the cavity, s = the area of the aperture, and S = the area of the interior surface of the blackbody including the aperture. Bedford's equation gives a minimum value for the effective emissivity of a cavity, while Gouffe's equation, which is exact for a spherical cavity, gives somewhat low values for other shapes. The higher of these two values was regarded as the better estimate. In addition, although the magnitudes of Ω , s and S can be determined with reasonable accuracy, the

spectral emissivity, ϵ , of the cavity inner wall must be estimated. The exact value of ϵ is difficult to determine. However, an estimate based on known values for metals and oxides gave an effective emissivity of 0.98 ± 0.01 for the blackbody cavities used.

The reflectivity of the mirror, ρ , was calculated using the equation³⁷

$$\rho = \exp\left[\left(\frac{1}{T_d} - \frac{1}{T_r}\right) \frac{C_2}{\lambda}\right] . \quad (3)$$

Here T_d is the temperature (K) measured when the pyrometer is sighted directly at the lamp, T_r is the temperature (K) measured when the pyrometer is sighted at the mirror, C_2 is the second radiation constant ($14388 \mu\text{m K}$), and λ is the wavelength ($0.65 \mu\text{m}$) measured by the pyrometer. Each of the pyrometer readings was determined for five lamp temperatures ranging from 1283 K to 1674 K. The reflectivity of the mirror was determined to be 0.873 ± 0.007 . The actual melting point, T , was then calculated using 0.98 for the effective emissivity and 0.873 for the mirror reflectivity and the equation

$$\frac{1}{T} = \frac{1}{T_r} + \frac{\lambda}{C_2} \ln(\epsilon_a \rho) . \quad (4)$$

The error in the melting point comes from three sources, the optical pyrometer reading, the reflectivity and effective emissivity values and the error in establishing the plateau. The error associated with the optical pyrometer,³⁸ ξ_1 , was based on National Bureau of Standards data;³⁹ the error in calculating the mirror reflectivity and cavity emissivity, ξ_2 , is a combination of both since ρ and ϵ_a are multiplied in Eq. (4). The error in the absolute value of their product, $\Delta\rho\epsilon_a$, is calculated by

$$\Delta\rho\epsilon_a = \pm\left(\frac{\Delta\rho}{\rho} + \frac{\Delta\epsilon_a}{\epsilon_a}\right), \quad (5)$$

where $\Delta\rho$ and $\Delta\epsilon_a$ signify the error in ρ and ϵ_a respectively. The error associated with the plateau temperature, ξ_3 , was determined by calculating the standard deviation from the mean of the points from the best straight line. The total error then is the square root of the sum of the squares of the individual errors.

To verify the performance characteristics of the technique and apparatus, the melting points of aluminum oxide and lithium fluoride were determined (Table II). The agreement of these experimental data with the accepted melting points, 2326 ± 3 K for aluminum oxide⁴⁰ and 1121 ± 2 K for lithium fluoride⁴¹ established the validity of the procedure.

Two separate batches of lithium oxide were used in the melting point determinations. The first analyzed to be 100.0% Li_2O and the second 99.8% Li_2O . Two runs were made on the first batch and three runs on the second. A typical cooling curve is shown in Fig. 1 and the results of the five runs are given in Table III. The standard deviation of ± 0.9 K for the error associated with locating the plateau regions demonstrates the excellent precision of the experimental technique. This combined with 3.4 K for the pyrometer calibration error ξ_1 and 2.8 K for the error associated with the mirror reflectivity and cavity emissivity ξ_2 gives a total error of ± 4.5 K. Thus we conclude that the melting point of lithium oxide is $1711 \text{ K} \pm 5 \text{ K}$.

(4) Additional Observations on the Properties of Lithium Oxide

(a) Corrosion. Moderate devitrification of a Pyrex reaction vessel occurred when lithium peroxide was decomposed at 633 K for 51 hours. This is 135 K lower than the temperature at which Rode and co-workers³⁷ first observed

TABLE II. MELTING POINT DATA FOR Al_2O_3 AND LiF

<u>Compound</u>	<u>MPt (K)</u>	<u>ξ_1</u>	<u>ξ_2</u>	<u>ξ_3</u>	<u>$\pm K$</u>
Al_2O_3	2327	5.0	4.0	0.0	6.4
LiF	1120.2	3.6	0.7	3.9	5.3
LiF	1121.7	3.6	0.7	3.8	5.3
LiF	1121.8	3.6	1.2	0.3	3.8

TABLE III. MELTING POINT DETERMINATIONS OF LITHIUM OXIDE

<u>Run</u>	<u>MPt (K)</u>	<u>$\xi_3 (\pm K)$</u>
1	1711.3	2.8
2	1710.7	0.5
3	1712.7	1.7
4	1711.6	0.9
5	1710.5	0.6
Mean	1711.4	0.9

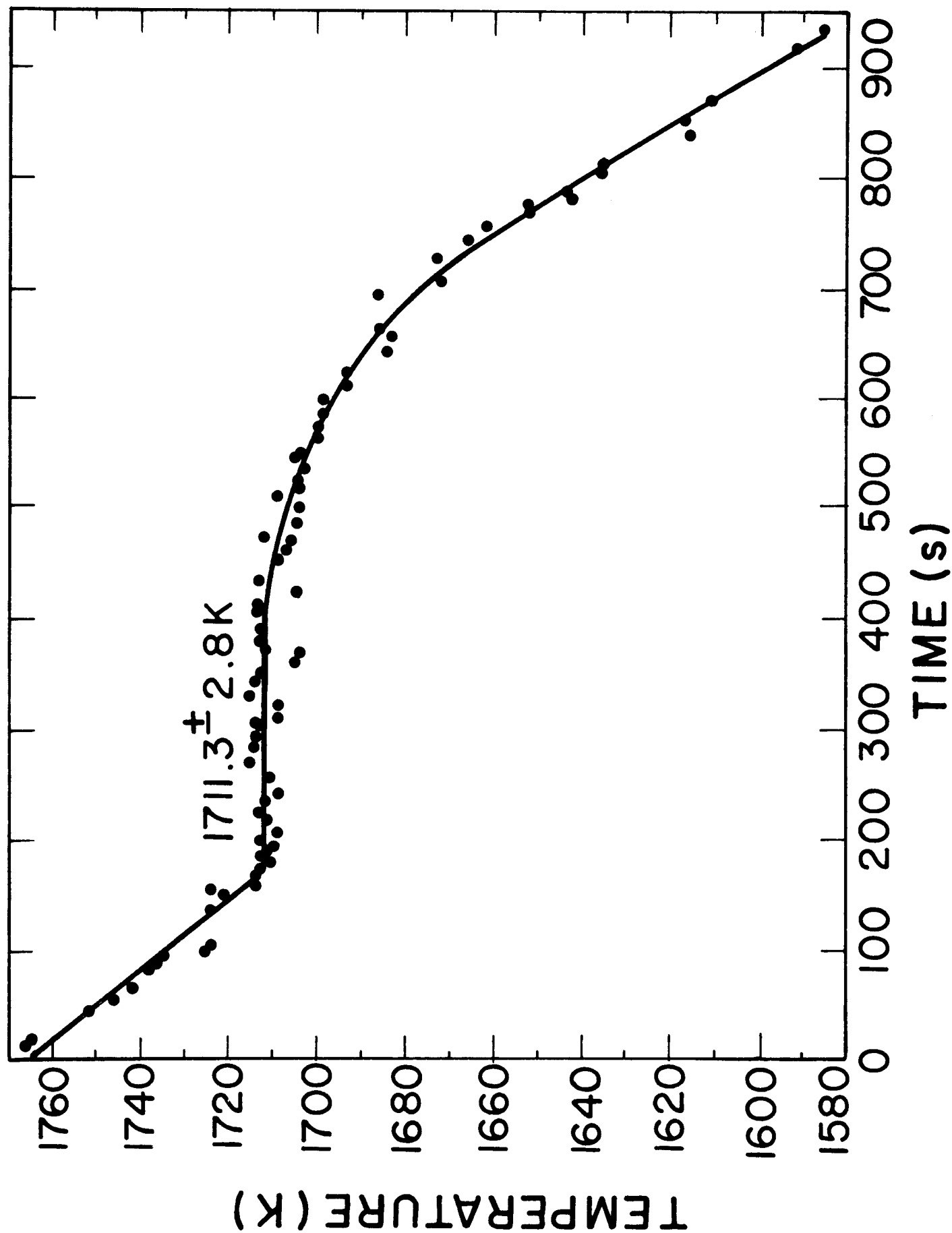


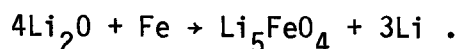
Fig. 1. Cooling Curve of Lithium Oxide.

attack of Pyrex by lithium oxide samples formed from the decomposition of lithium peroxide. One possible explanation for this discrepancy is that the experiments performed by Rode were of the order of 1 hour in duration while the one performed here was roughly 50 times longer. The reaction of lithium peroxide or oxide with silicon dioxide is exoenergetic even at room temperature, therefore, the kinetics must be such that reaction was not observed in the shorter experiments of Rode until the higher temperatures were reached. However, absolutely no attack was seen in this study when the temperature was 575 K for > 50 hours. As discussed previously, any hydroxide and carbonate impurities were decomposed by heating lithium oxide samples in a stepwise manner in a model vessel to > 1035 K. This stepwise decomposition process had the advantage of removing the hydroxide impurity at the lowest reasonable temperature, thus minimizing the corrosive action of lithium hydroxide. Nevertheless, the purification procedure proved to be a corrosive process. Metal reaction vessels could only be used satisfactorily for one synthesis. After this, either the vessel had to be disposed of or a clean surface had to be regenerated by machining. When using 304 stainless steel vessels, the lithium oxide sample-stainless steel reaction zone invariably contained Li_5FeO_4 . In cases of severe reaction, LiCrO_2 was also observed. These results are markedly similar to those found Kurasawa and co-workers^{42,43} in compatibility studies of lithium oxide with 304 and 316 stainless steels.

The synthetic results obtained here suggest that the hydroxide, and possibly carbonate, impurities in lithium oxide may play a major role in its corrosion with reaction vessels. Additional support for this hypothesis came from the following experiment. Fused, ground and sieved (< 200 μm diameter) 99.5% pure lithium oxide (0.4% lithium hydroxide and 0.05% lithium carbonate

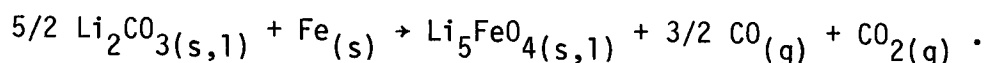
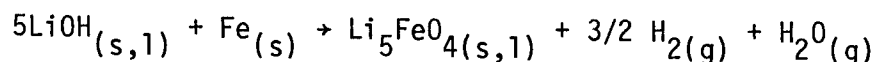
impurities) was reheated in a 304 stainless steel container under a dynamic vacuum of 0.3 Pa at temperatures from 915 to 1060 K for 60 hours and then at 1060 K for 120 hours. The attack by the sample on the stainless steel was slight and no Li_5FeO_4 could be detected at the sample-stainless steel interface by x-ray powder pattern analysis. However, there was probably a small quantity of an iron bearing compound in the sample since the region where the sample had contacted the stainless steel was slightly gray and when this part of the sample was dissolved in dilute hydrochloric acid the resultant solution was light yellow. Nevertheless, the degree of reaction between the 99.5% pure lithium oxide sample and the stainless steel container was markedly less than seen in the case of less pure samples. The low reactivity of this sample is undoubtedly due to its low concentration of hydroxide and carbonate. The fact that the sample reacted at all with the stainless steel may have been due to the one-half percent of impurities and not to any intrinsic reactivity on the part of the lithium oxide.

Despite this influence of impurities, none of the studies concerned with the corrosion properties^{42,43} or reactivity^{44,45} of lithium oxide have used well characterized samples in which the carbonate and hydroxide levels were known. Thus, the qualitative similarity found in this study and that of Kurasawa may indicate that their lithium oxide was not 100% pure. For example, they explain that the presence of the Li_5FeO_4 corrosion product is due to the reaction



However, based on the preceding discussion and the absence of analytical data

on the purity of their lithium oxide, it seems that the presence of Li_5FeO_4 is more likely due to reduction of hydroxide or carbonate as given by



The free energies calculated from JANAF data² and data from Takeshita et al.⁴⁶ for the oxidation of iron to Li_5FeO_4 by lithium oxide, hydroxide and carbonate are given in Table IV. For the conditions described, lithium hydroxide is the only compound that will act as an oxidizing agent.

Several preliminary melting point experiments also provided evidence of the extreme reactivity of impure lithium oxide samples. A lithium oxide sample, 97.0% pure containing 1.3% lithium hydroxide and 1.7% lithium carbonate was heated in a graphite crucible to 1770 K. After cooling, the sample was observed to be gray rather than white in color and to have attacked the crucible, causing it to crack in several places. A carbonate analysis indicated that the lithium carbonate impurity level had dropped to 0.03%. X-ray powder patterns showed only the presence of lithium oxide and trace quantities of lithium acetylide. Lines due to lithium hydroxide and lithium carbonate had disappeared.

A lithium oxide sample 86.2% pure containing 12.6% lithium hydroxide and 1.2% lithium carbonate melted through a tantalum crucible when heated to 1600 K. X-ray powder patterns of the residue showed the major phases to be Li_7TaO_6 and lithium oxide. No lines due to either lithium hydroxide or lithium carbonate were observed.

TABLE IV. THERMODYNAMIC DATA FOR THE FORMATION OF Li_5FeO_4

Reaction	ΔG (kJ)		
	800 K	1000 K	1200 K
$4\text{Li}_2\text{O}(\text{s}) + \text{Fe}(\text{s}) \rightarrow \text{Li}_5\text{FeO}_4(\text{s}) + 3\text{Li}(\text{g})$	627	553	480
$4\text{Li}_2\text{O}(\text{s}) + \text{Fe}(\text{s}) \rightarrow \text{Li}_5\text{FeO}_4(\text{s}) + 3\text{Li}(\text{l})$	395	378	360
$5\text{LiOH}(\text{l}) + \text{Fe}(\text{s}) \rightarrow \text{Li}_5\text{FeO}_4(\text{s}) + 3/2 \text{H}_2(\text{g})$ $+ \text{H}_2\text{O}(\text{g})$	21	2	-15
$5/2 \text{Li}_2\text{CO}_3(\text{s,l}) + \text{Fe}(\text{s}) \rightarrow \text{Li}_5\text{FeO}_4(\text{s}) + 3/2 \text{CO}(\text{g})$ $+ \text{CO}_2(\text{g})$	220	150	104

Finally, a lithium oxide sample, 80.5% pure containing 16.0% lithium hydroxide and 3.5% lithium carbonate melted through a tungsten crucible when heated to 1770 K. No carbonate was detected in the melted product by infrared analysis. X-ray powder patterns did not show the presence of either lithium hydroxide or lithium carbonate. While the major phase present was still lithium oxide, significant quantities of Li_6WO_6 had been formed. This experiment can be contrasted with one conducted in which 99.8% pure lithium oxide was successfully melted in a tungsten crucible. Negligible attack of the crucible occurred. X-ray powder patterns showed detectable quantities of Li_6WO_6 but the total tungsten concentration was measured by neutron activation analysis to be 0.7%. The preceding results reinforce the conclusion derived from synthetic observations that major high temperature handling problems of lithium oxide are due to hydroxide and carbonate impurities.

(b) Sintering. The common feature of all sintering processes is the diminution of the surface area of an assembly of particles; the driving force for this process is a diminution of the surface energy which accompanies the loss of surface area.⁴⁷ The six stages of sintering have been described by Hirschhorn⁴⁸ as:

- (1) initial bonding among particles,
- (2) neck growth,
- (3) pore channel closure,
- (4) pore rounding,
- (5) densification or pore shrinkage, and
- (6) pore coarsening.

Sintering was observed in a number of preparations of lithium oxide.

Scanning electron micrographs of lithium oxide from three different syntheses exhibit different stages in the sintering process. The micrographs show that material heated only at low temperatures, < 681 K, for a total of 25 hours indicate that little or no sintering occurred. A high magnification micrograph ($\times 2000$) demonstrates that the particles have retained their individual integrity.

Micrographs taken of material after the peroxide has been decomposed by heating for 20 hours at 585 K, 5 hours at 681 K, 17 hours at 775 K, 24 hours 868 K, 7 hours at 1020 K, and finally, 36 hours at 1060 K show bonding between particles, neck growth and the formation of grain boundaries in the original neck areas.

The micrographs taken of material which had been heated at temperatures above 1000 K for a longer period (183 hours) show that an advanced stage of sintering is present. Many small pores and grain boundaries are present in the low magnification micrograph ($\times 200$). In the high magnification micrograph ($\times 600$), a single triangular pore is present while nearly circular ones surround it, indicating that pore rounding has proceeded almost to completion. The density of this material was measured pycnometrically as 1.90 ± 0.03 g/cm³, or 94% of theoretical density.

An estimate of the sintering temperature of lithium oxide has been made as 1183 K.^{5,49} The sintering observed in these experiments occurred at temperatures more than 100 K lower than this. However, it is possible that the impurities remaining in the original lithium oxide samples, which were obtained from the low temperature decomposition of lithium peroxide, contributed to its sintering characteristics. For example, there is evidence that water given off by the decomposition of hydroxides may activate the sintering

process in oxides.⁵⁰ For this reason, the 99.5% pure, fused lithium oxide particles were examined for sintering after having been heated at temperatures from 915 to 1060 K for 60 hours and then at 1060 K for 120 hours. Scanning electron micrographs of the sample were taken before and after heating. Before heating the particles were loose, and after heating they were in the form of a cluster, though the cluster could be relatively easily broken apart into smaller clusters. This indicated initial bonding among particles. The micrographs after heating show particles in which the edges are somewhat rounded while the particles before heating have sharper edges. This result is consistent with the onset of sintering and a diminution of the surface area of the particles. Neck growth between two particles is observed in a high magnification micrograph (x 540). Thus it can be stated that, although the particles were arrested in an early stage in the sintering process, sintering appeared to be occurring. This experiment still does not answer the question of whether 100% pure lithium oxide sinters at a temperature of 1060 K, but it does point out that even highly pure (99.5%) lithium oxide appears to sinter at this temperature.

This result has important implications concerning the use of lithium oxide as a solid breeder in proposed nuclear fusion reactors. Sintering is undesirable as it would slow the diffusion of tritium out of the breeder by increasing the diffusion path length. The result would be a high tritium inventory in the breeder.

(c) Colored Samples. An intriguing result obtained in these experiments was the occasional production of blue lithium oxide. A common characteristic of this blue lithium oxide was the disappearance of the color upon standing in air for several days or upon heating on a hot plate.

The existence of colored specimens of normally colorless materials is due to structural imperfections where the imperfections are the result of lattice defects or impurity atoms.^{51,52} These colorations produced by various means are due to centers formed by the trapping of electrons or holes at lattice defects. Generally, these color centers are produced by the diffusion of the species of either the corresponding cation or anion into the lattice, by electrolytic processes producing non-stoichiometric crystals, by ionizing radiation or by introduction of impurity atoms.⁵² Thus, the observation of color centers in lithium oxide during its thermal purification does not represent a customary production technique.

Optical absorption spectra of blue lithium oxide shows considerable similarity between the spectra obtained in this experiment and that of Uchida⁵³ for neutron irradiated lithium oxide. This suggests that similar imperfections are introduced into the lattice during the thermal decomposition of the lithium hydroxide and/or carbonate. Uchida et al. assigned the band at 310 nm to the presence of F centers (oxide vacancy occupied by an electron). The bands they observed at 375 and 570 nm in the heavily irradiated specimens were speculated to be associated with aggregate F centers. They had no assignment for the band appearing at 425 nm in the most strongly irradiated specimen. In the spectrum obtained here on the blue lithium oxide, a band is definitely present at between 560 and 570 nm, a shoulder appears to be present in the 400 to 410 nm region and the absorbance at ~ 320 nm is very strong. This spectrum coupled with the results obtained by Uchida et al. suggest that F centers have been produced in lithium oxide by the thermal purification. It is intriguing that imperfections in the lithium oxide lattice can be produced by thermal

decomposition of the hydroxide and/or carbonate impurities as well as by irradiation effects.

Acknowledgement

This work was initiated under a contract with the Electric Power Research Institute and the Fusion Engineering Program of the University of Wisconsin-Madison. The authors thank Mr. G.D. Nutter of the Instrumentation Systems Center of the College of Engineering for providing the equipment and the instruction in the techniques of making high temperature measurements. The authors also thank Kathleen Plute for her contributions to the composition and editing of this manuscript. We are indebted to Kevin Okula for the neutron activation analyses and scanning electron micrographs.

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THE PREPARATION AND MELTING POINT OF OCTALITHIUM ZIRCONATE

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ABSTRACT

Octalithium zirconate was prepared by heating a pelletized stoichiometric mixture of fused lithium oxide and zirconium dioxide under a dynamic vacuum up to a temperature of 863 K for 40 hours. The melting point was determined to be 1568 ± 5 K. The chemical inertness and high lithium atom density, 5.93×10^{22} atoms/cm³, make octalithium zirconate a candidate for a solid tritium breeder.

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I. Introduction

Three compounds are known in the lithium oxide-zirconium dioxide system. They are dilithium zirconate, Li_2ZrO_6 , tetralithium zirconate, Li_4ZrO_4 , and octalithium zirconate, Li_8ZrO_6 .^{1,2} The use of octalithium zirconate as a breeder in fusion reactors has never been studied in contrast to dilithium zirconate.^{3,4} It is clear that one of the reasons for the lack of interest in octalithium zirconate, despite its high lithium atom density, is the lack of data on its properties. In particular, its melting point is not known. Therefore, the melting point of octalithium zirconate was measured in this work as a necessary first step towards determining whether it has potential as a tritium breeding material.

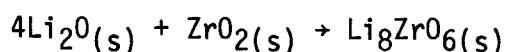
Octalithium zirconate was first synthesized by Scholder et al.¹ by heating lithium oxide and zirconium dioxide together in a four to one mole ratio for 12 hours at 773 K and for an additional 5 hours at 823 K. Belyaev and Annopol'skii² heated a lithium hydroxide-zirconium dioxide mixture in a mole ratio of eight to one for 20 hours at 1223 K and observed that octalithium zirconate was present in the product. However, attempts to synthesize octalithium zirconate by reacting lithium carbonate with zirconium dioxide were unsuccessful. Belyaev and Annopol'skii stated that heating lithium carbonate with zirconium dioxide at 823-1023 K for one hour led to the formation of dilithium zirconate irrespective of the original reagent ratio. This is somewhat inconsistent with the results of differential thermal analysis experiments performed on mixtures of lithium carbonate and zirconium dioxide with mole ratios as high as five to one in which they observed two endothermic peaks. The first at about 1000 K was attributed to the formation of dilithium zirconate. Although the mixtures were heated to 1233 K, the formation of octalithium zirconate was

not observed. Plyushchev and Grizik⁵ heated mixtures of lithium carbonate and zirconium dioxide with mole ratios as high as six to one at temperatures of 1073-1473 K and produced only dilithium zirconate.

II. Experimental

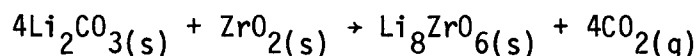
(1) Synthesis

Fused lithium oxide from previous melting point determinations⁶ and zirconium dioxide (chemically pure, E.H. Sargent, Chicago, IL), in a 4:1 stoichiometric mole ratio



were mixed by grinding in an inert atmosphere. The mixture is pressed into a pellet and heated in a platinum boat in vacuo for 24 hours at 863 K. The mixture was reground, a small quantity removed for an x-ray powder pattern, repelletized and heated for another 16 hours at 863 K. Powder patterns were taken as described elsewhere.⁶ The lines measured (Table I) were compared with the JCPDS file data⁷ for Li_8ZrO_6 . Lines not previously reported were indexed on the basis of the hexagonal system.

The synthesis of octalithium zirconate by the reaction



was studied by grinding stoichiometric quantities of the two components, pelletizing, weighing and then heating the pellets at 973 K in a flowing nitrogen stream for 26 hrs. The pellets were weighed, reground, a sample taken for an x-ray powder pattern, the pellet reformed, and again heated. This procedure

Table I. X-Ray Power Pattern of Octalithium Zirconate (Li_8ZrO_6)

This Study		Reference ⁵		This Study		
d (Å)	d (Å)	Intensity	hkl	d (Å)	Intensity ^(a)	hkl
5.16	5.15	40	003	1.167	10	<u>1112</u> , 309
4.55	4.52	100	101	1.131	2	137, 404
4.05	4.04	50	012	1.110	3	<u>1211</u>
2.998	2.996	20	104	1.091	2	318, 321
2.745	2.744	3	110	1.072	3	<u>0114</u> , 229
2.589	2.583	20	015, 006	1.046	2	407, 324
2.421	2.419	80	113	1.030	< 2	<u>0015</u>
2.342	2.351	13	021	1.019	5	413, 143
2.265	2.268	12	202	1.001	3	<u>3012</u> , <u>1310</u>
2.019	2.021	10	024	0.979	2	327
1.999	2.003	10	107	0.961	15	<u>3111</u> , 416+
1.875	1.875	75	205, 116	0.950	3	502, 051
1.783	1.785	25	018, 211	0.941	2	<u>1214</u> , <u>2212</u>
1.747	1.748	18	122	0.914	< 2	330
1.715	1.716	4	009	0.900	< 2	333, 241
1.627	1.627	18	214	0.887	3	<u>1313</u> , 419+
1.618	1.617	9	027	0.875	< 2	244
1.585	1.583	30	300	0.863	4	425, 336
1.552	1.552	15	125	0.852	2	<u>2116</u> , 511
1.511	1.513	11	303	0.848	< 2	<u>3114</u> , 152
1.497	1.498	7	208	0.832	< 2	514, 247

1.469	1.470	5	1010	0.822	2	1118, 155
1.455	1.456	18	119	0.808	3	1217, 339+
1.391	1.393	11	217	0.795	< 2	517
1.369	1.371	2	220	0.783	2	158,431
1.345	1.348	7	306, 0111			
1.325	1.325	10	223			
1.312	1.314	16	128,131			
1.300	1.300	10	312, 0210			
1.289	1.287	4	0012			
1.246	1.248	5	134			
1.210	1.210	18	315, 226+			
1.183	1.185	4	401			

(a) Estimated visually.

was repeated three times with the heating temperatures and duration of heating being 973 K for 15 hours, 1023 K for 19 hours and 1023 K for an additional 11 hours. The 25 most intense d spacings in each powder pattern corresponding to each of the four heating stages were assigned to the reactants and di, tetra, or octalithium zirconate.

(2) Density Measurements

Density measurements were made on fused, crystalline octalithium zirconate by water displacement in a pycnometer at 25°C. The experimental density is $2.99 \pm 0.01 \text{ gm/cm}^3$. The density based on the unit cell dimensions⁷ for $n=3$, is 3.01 g/cm^3 .

(3) Melting Point Measurements

Three melting point determinations were run as described.⁶ The first determination was made using the fused products of the previous two runs. Sample weights were 14.5, 18.1 and 25 grams. All three runs were performed in platinum crucibles. The effective emissivity of the cavity was calculated to be 0.99. A representative cooling curve is shown in Fig. 1.

III. Discussion

(1) Synthesis

The synthesis of octalithium zirconate using lithium oxide as starting material was quantitative under the conditions described. The synthesis using lithium carbonate as starting material was not as successful. The progress of this reaction as followed by x-ray powder patterns showed certain trends. As expected, the lines attributable to lithium carbonate and zirconium dioxide decreased in relative intensity throughout the four heating stages. In fact, by the end of the second heating stage, lines due to zirconium dioxide were no longer present though ones due to lithium carbonate persisted even after the

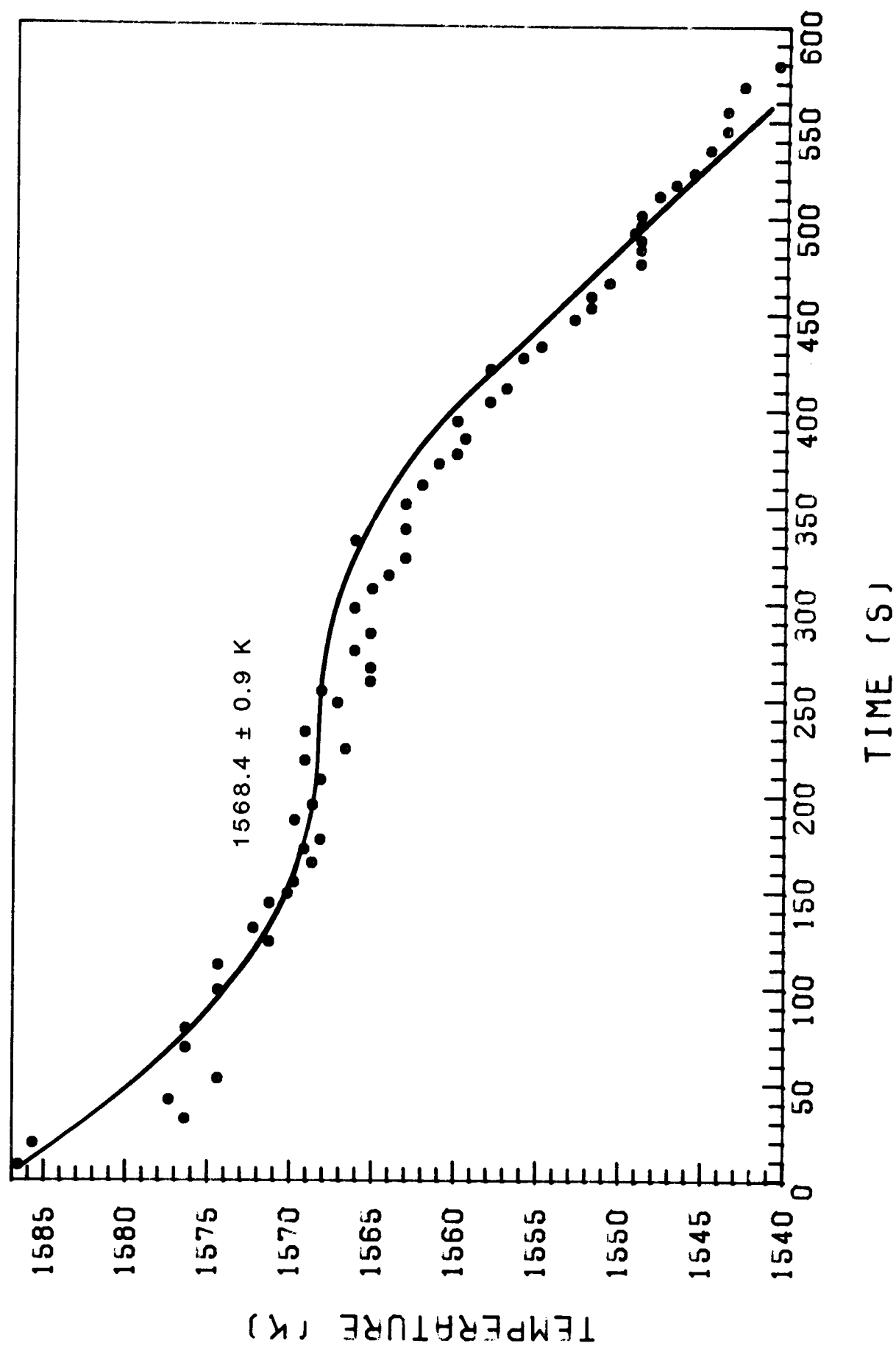
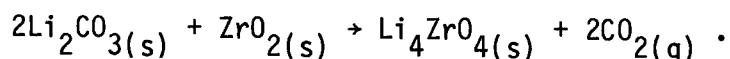
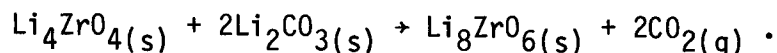


Fig. 1. Cooling Curve of Octalithium Zirconate.

final heating. A somewhat unexpected result was the formation of substantial quantities of tetralithium zirconate in the early heating stages. This is consistent with the disappearances of lines due to zirconium dioxide at the end of the second heating stage by the reaction



It was not until after the final heating stage that the lines attributable to octalithium zirconate were of comparable intensity to those of tetralithium zirconate. It seems likely that the formation of octalithium zirconate involves, at least to a limited extent, the reaction



Furthermore, it is possible that dilithium zirconate is formed in the early stages of heating and that it reacts further in a stepwise fashion through the lower lithium zirconates until octalithium zirconate is reached.

Data on the weight loss of a pellet after each heating stage are consistent with the trends observed in the powder pattern intensity data. The cumulative weight loss after each heating was 13.7%, 18.5%, 26.6%, and 30.6%, respectively. Since complete conversion to octalithium zirconate would involve a weight loss of 42.0% and formation of pure tetralithium zirconate a loss of 21.0%, the data seem to indicate that after the final heating stage, there were, in very approximate terms, equal concentrations of tetralithium zirconate and octalithium zirconate. These results show that octalithium zirconate does form in lithium carbonate-zirconium dioxide mixtures with molar ratios $> 4:1$

contrary to previously published results. This may be due to the longer reaction time used here compared with the reaction times used in other work.^{2,5} However, despite the convenience of using lithium carbonate as a starting material, the synthesis of octalithium zirconate using lithium oxide starting material was so successful that additional experiments using the carbonate were not pursued.

(2) Melting Point

The analysis of the cooling curves for the three runs gave melting points of 1568.4 K, 1570.3 K and 1563.1 K, with a mean of 1567.6 K and an uncertainty (ξ_3) in the plateau determination of ± 3.2 K. The pyrometer calibration error (ξ_1) was ± 3.2 K and the error for the mirror reflectivity and cavity emissivity (ξ_2), ± 1.1 K, giving a total error of ± 4.7 K. To four significant figures the corrected melting point is 1568 ± 5 K.

Although the total error associated with the melting point determination of Li_8ZrO_6 is essentially the same as obtained for Li_2O , the magnitudes of the component contributions differ. The larger error in determining the plateau region, ± 3.2 K for Li_8ZrO_6 compared to ± 0.9 for Li_2O , negates the lower errors for ξ_1 and ξ_2 and results in a somewhat less precise melting point for Li_8ZrO_6 than obtained for Li_2O .⁶

(3) Octalithium Zirconate as a Tritium Breeder

We suggest that octalithium zirconate be added to the list of possible tritium solid breeders (Table II). The melting point and lithium atom density of the octalithium zirconate both are lower than the corresponding values for lithium oxide. However, the octalithium zirconate is stable with respect to water vapor and carbon dioxide, at least at room temperature, whereas lithium

Table II. Some Properties of Oxide Candidates for a Tritium Solid Breeder

Breeder	Melting Point (K)	Density (g/cm ³)	Lithium Density (10 ²² atoms/cm ³)
Li ₂ O	1711	2.02	8.16
LiAlO ₂	1883	2.55	2.33
Li ₅ AlO ₄	1320	2.22	5.34
Li ₂ SiO ₃	1474	2.52	3.38
Li ₄ SiO ₄	1529	2.39	4.81
Li ₂ TiO ₃	1820	3.46	3.80
Li ₂ ZrO ₃	1873	4.15	3.27
Li ₈ ZrO ₆	1568	2.99	5.93

oxide reacts rapidly with both. The chemical inertness of the zirconate compared to the reactivity of the oxide, is a distinct advantage for the former.

Octalithium zirconate occupies a unique position among the ternary oxides. Not only is its lithium atom density the highest of any ternary oxide, but its melting point is also reasonably high. In particular, octalithium zirconate offers substantial benefits over the silicates which have been proposed as breeders^{10,11} since it has a higher melting point and a significantly higher lithium atom density than do any of the lithium silicates. Octalithium zirconate appears to be quite stable with respect to decomposition at its melting point. X-ray powder patterns obtained on fused samples show no evidence for decomposition to lower lithium containing zirconates. However, powder patterns of the zirconate which had been heated to 200 degrees beyond its melting point did show lines due to tetralithium zirconate. No lines attributable to lithium oxide were present. It is clear that some thermal decomposition occurs in the vicinity of the melting point, for mass spectroscopic⁹ examination of the vapor phase species at about 1600 K shows the presence of gaseous lithium and oxygen. We conclude that octalithium zirconate should be given consideration as a potential tritium breeding material in nuclear fusion reactors, and its properties such as thermal conductivity, tritium diffusion, phase stability and structure should be studied in detail.

Acknowledgement

This work was supported in part by the Fusion Engineering Program, Nuclear Engineering Department, the University of Wisconsin, Madison, WI. The authors thank Mr. G.D. Nutter of the Instrumentation Systems Center of the College of Engineering for providing the equipment and instruction in the technique of

making high temperature measurements. The authors also thank Kathleen Plute for her contributions to the composition and editing of this manuscript.

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