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EFFECTS OF FAST NEUTRON IRRADIATION ON THERMAL CONDUCTIVITY OF Li_2O and $LiAlO_2$

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1. Abstract

Li_2O and $LiAlO_2$ are two candidates for solid breeder materials in the United States' Fusion Power Program. Critical to breeder design efforts are thermophysical data, the bulk of which have only recently become available, for unirradiated lithium ceramics[1-5]. This paper expands the current limited database by presenting thermal conductivity data between 373-1173K for both materials following fast neutron irradiation. Samples were irradiated at 773-1173K to lithium burnups $\leq 11.5 \times 10^{20}$ captures/cm^3. Comparisons are made between these data and those from unirradiated archive samples of these same materials.

2. Introduction

One of the more significant components related to the economic and safe operation of current fusion reactor designs is the blanket from which, tritium is generated and recycled to the reactor for use as fuel. The technology development programs for solid breeder materials are in their

infancy compared to those for light-water and liquid-metal reactor fuels and blankets. Hence, there are very few thermal properties data available for candidate fusion blanket materials, and even less under prototypic irradiation conditions. It was therefore the purpose of this investigation to provide a small, but significant database relating to the change in thermal conductivity of Li_2O and $LiAlO_2$ due to prototypic, high-temperature irradiation environments. Presented are thermal conductivity data derived from thermal diffusivity measurements via the flash-method described by Parker, et. al.[6] Samples were taken from pellets irradiated in the Hanford Engineering Development Laboratory's FUBR-1A experiment previously described in detailed by Hollenberg[3,7-9].

3. Experiment Description

Pellets (0.95-cm diameter) of lithium aluminate and lithium oxide, all at approximately 85% TD, were irradiated in sealed capsules in the Experimental Breeder Reactor No. 2 (EBR-II). These materials were irradiated at three different temperatures and reactor exposures, resulting in three different lithium burnup levels. Table 1 shows a partial material test matrix giving the irradiation temperatures and lithium burnups for each sample. Results of various measurements on representative samples of these materials were reported in the literature, including burnup[8], retained tritium[10] and swelling[9]. Thin cylindrical samples (<0.076-cm thick) were cut from pellets using a diamond wafering blade. Extreme care was necessary in cutting and handling the samples since nearly all of the pellets were severely

cracked. Where possible, diffusivity samples were cut from the middle of the short four-pellet column to avoid the effects of the high temperature gradient present at the ends of the pellet column during irradiation.

TABLE 1

PARTIAL FUBR-I MATERIAL TEST MATRIX

MATERIAL	IRRADIATION TEMPERATURE (K)	APPROXIMATE LITHIUM BURNUP (10^{20} capts/cm^3)	REACTOR EXPOSURE (FPD)
Li_2O, $LiAlO_2$	773	4.0, 3.0	105
Li_2O, $LiAlO_2$	973	4.0, 3.0	105
Li_2O, $LiAlO_2$	1173	4.0, 3.0	105
Li_2O, $LiAlO_2$	773	7.0, 5.5	192
Li_2O, $LiAlO_2$	973	7.0, 5.5	192
Li_2O, $LiAlO_2$	1173	7.0, 5.5	192
Li_2O, $LiAlO_2$	773	11.5, 8.5	297
Li_2O, $LiAlO_2$	973	11.5, 8.5	297
Li_2O, $LiAlO_2$	1173	11.5, 8.5	297

Since the samples contained tritium, measurements were conducted in an air-tight chamber (see Figure 1). The exterior of the chamber was cooled with flowing water to prevent diffusion of tritium through the chamber walls and release to the laboratory environment. The radiological hazards required all sample preparation, positioning and loading to be conducted in a hot cell filled with dry helium. Following sample loading, the test chamber was back-filled with helium to 300 Torr at room temperature, and then transferred into an adjacent laboratory where the diffusivity measurements were made.

Located within the chamber was a small electric furnace to provide measurements at various temperatures. The nickel-chrome element furnace

(1000 Watts) allowed temperatures greater than 1273K to be achieved (though other restrictions prevented taking measurements above 1173K) in the test chamber. The energy pulses was provided by an Apollo Ruby, Model 22 laser (30 Joules - 800 microsecond pulse). The pulse penetrated the test chamber via a sapphire window (see Figure 1). Energy from the back surface of the samples radiated through a second sapphire window located at the top of the test chamber, was focused through two CaF_2 lenses, and detected using a liquid nitrogen-cooled InSb infrared detector. The signal from the detector was recorded with a Tektronix 7704A oscilloscipe, digitized by a Tektronix P7001 Digitizer and analyzed by a Tektronix 4052 minicomputer. The time required to reach half the maximum temperature rise on the back surface of the sample was determined from a least-square fit of the temperature waveform.

To maximize absorption of the laser energy, both surfaces of each sample were coated with thin layer of metallic silver. In most cases, diffusivity measurements were taken at 100K increments beginning at 373K to a maximum temperature of 1173K. Generally, five measurements were made at each temperature to provide good statistical analyses. Typical error estimates are given with the data presented below. Measurements were also taken on several samples during cool-down (from 1173K).

4. Discussion

Parker, et. al.[6] discussed the flash-method for determining thermal

diffusivity (and thermal conductivity). In general, thermal conductivity is calculated from experimentally-measured thermal diffusivity:

$$\alpha = 1.38 * DC * L^2 / \pi^2 * t_{1/2} \qquad (1)$$

where, α = thermal diffusivity,
D = density,
C = heat capacity,
L = sample thickness, and
$t_{1/2}$ = time required for rear surface to reach one-half its maximum value.

Equation 1 assumes constant material properties, uniform sample heating, and no heat losses. To account for differences between the ideal and real cases, the technique was modelled using the heat transfer computer code HEATING5[11]. Radiation and other sources of heat loss (gas conduction and conduction to sample holders) were modelled. The thin, infrared-absorbing silver coating was also included in the model. These temperature-dependent effects were accounted for in Equation 1 by adjusting the $t_{1/2}$ determined from experiment. The required adjustment ranged from -12.9% at 373K to +7.0% at 1173K.

ARMCO iron was used as a standard to confirm the experiment technique used during data collection. Measured data followed the recommended values reported by Touloukian[12] to within less than 5%.

Measured results from unirradiated archive samples of Li_2O and $LiAlO_2$ are compared in Figures 2 and 3 with those of Takahashi[2], and Schulz[5], Gurwell[1], and Rasneur[4], repectively. In both cases, measured data

were fit (least squares) to the $k = 1/(AT+B)$ functional form, where T is absolute temperature, and A and B are constants characteristic of the material. Data reported at porosities greater than zero were adjusted to 100% density for consistency using the Maxwell-Eucken equation, $(1-P)/(1-\beta P)$, where P is porosity and β is the pore correction factor as discussed by Takahashi.

For lithium oxide (Figure 2), the data show a steeper slope at low temperature, and nearly equal slope at high temperatures compared to Takahashi. However, at high temperatures, Takahashi's data is slightly higher.

Comparison of the measured lithium aluminate data with those of Schulz is excellent (Figure 3), though Gurwell and Rasneur report lower values at all temperatures. The good comparison of measured data with literature values, especially in the case of lithium aluminate, support the results of the irradiated samples given below. Except for effects associated with irradiation, i.e., high irradiation temperatures, retained tritium, swelling, etc., the irradiated and unirradiated archive samples were nearly identical.

Lithium Oxide

Figures 4,5, and 6 show the measured thermal conductivity data as a function of temperature for lithium oxide irradiated at 773, 973 and 1173K to 105, 192, and 297 FPDs, respectively. The curve derived from

the unirradiated data is included for comparison. Data from irradiated samples generally follow the characteristic 1/(AT+B) trend. No differences were observed between the data collected during heat-up and cool-down. The distinction between different irradiation temperatures is apparent in these data at low measurement temperatures. However, the data at all irradiation temperatures approach similar, low values of conductivity at high measurement temperatures.

In general, all of the measured thermal conductivity data were lower than the unirradiated values. Conductivity values for the sample irradiated at 1173K are reasonably consistent, showing lower values with increasing burnup - a manifestation of increased damage due to irradiation. However, data from the sample irradiated at 773K (Figure 6) to high burnup (297 FPD) is drastically different. The latter data are close to unirradiated values suggesting little influence of burnup. This "lack of influence" is explained by grain size.

Because grain boundaries offer increased scattering centers for phonons, materials with larger grain sizes can have high thermal conductivities. Hollenberg[7] reported grain sizes for those samples irradiated to lithium burnups of 4×10^{20} capts/cm^3. He observed significant grain growth in lithium oxide at 1173K, but very little at 773 or 973K. Similar results were observed for samples irradiated to higher burnup levels as shown in Table 2, except for Li_2O irradiated at 773K to 11.5×10^{20} capts/cm^3 (Hollenberg's results are included for

completeness). The large grain size observed in this sample explains the higher thermal conductivities values observed in Figure 6.

TABLE 2

OBSERVED AVERAGE GRAIN SIZE

SAMPLE	IRRADIATION TEMPERATURE (K)	BURNUP (10^{20} capts/cm^3)	AVGERAGE GRAIN SIZE (μm)*
Li_2O	773	4.0	3.4°
Li_2O	973	4.0	7.1°
Li_2O	1173	4.0	17.1°
Li_2O	773	7.0	5.8
Li_2O	973	7.0	7.2
Li_2O	1173	7.0	14.4
Li_2O	773	11.5	11.3
Li_2O	973	11.5	6.7
Li_2O	1173	11.5	16.3
$LiAlO_2$	773,973,1173	3.0,5.5,8.5	<1.0

* Determined by Linear Intercept Method.
° From Reference 7.

For the oxides, the average grain size increased at all burnup levels with increasing irraditation temperature, except the 773K, high lithium burnup sample. The abnormally-large relative grain size for this case is yet unexplained. However, if the observed grain sizes from Table 2 are compared at similar temperatures, only the 773K data show a statistically significant increase. The 973K and 1173K data, respectively, display a relatively constant grain size, within the estimated error of measurement. This suggests that an equilibrium grain size was achieved within the pellets during irradiation prior to reaching a lithium burnup of 4×10^{20} capts/cm^3. Preirradiation grain sizes for all of the oxide samples were reported to be within the range of 2 to 10 μm[13]. Perhaps the 773K pellet irradiated to high burnup experienced an unexpected

overtemperature environment in-reactor. The larger grain size (fewer grain boundaries) of this sample helps explain why the the measured conductivity is so high compared to the other samples at the same burnup level. The effect of grain size on conductivity has obscured the effect related to irradiation damage.

At low burnup (105 FPDs), the sample irradiated at 973K also showed a relatively high thermal conductivity at low measurement temperatures (Figure 4). It is not obvious why this particular sample should have a high thermal conductivity. Baldwin[10] has shown that similar material from this same capsule retained significantly more helium and tritium than other samples at the same burnup which were irradiated at different temperatures. Significant volumetric swelling (8%) was also observed[9] for similar material from the same capsule relative to the other samples. Resolution of these inconsistent results may explain the unexpectedly high thermal conductivity of this sample.

Lithium Aluminate

The thermal conductivity of the lithium aluminate material displayed an interesting response to temperature. In comparing Figures 7-9, which show thermal conductivity results of measurements for the lithium aluminate samples during the heat-up phase (where the measurement temperature was raised from room temperature to the maximum temperature), the thermal conductivity for all of the samples is nearly constant, about 3-4 W/m-K for all irradiation temperatures and lithium burnups

considered. Data collected during this phase suggests a saturation of the thermal conductivity similar to observations made by Tam[14] and Hurley[15] for other materials at high measurement temperature. This behavior was expected since it is known that the phonon mean free path decreases with temperature and irradiation damage. From the kinetic theory of gases, the thermal conductivity can be estimated by:

$$k = 1/3 * C * v * l \qquad (2)$$

where,
- k = thermal conductivity,
- C = heat capacity,
- v = average phonon velocity in the lattice, and
- l = average phonon mean free path.

The average phonon mean free path is given by:

$$1/l = 1/l_{phonon} + \sum 1/l_{defects} \qquad (3)$$

where,
- l_{phonon} = phonon mean free path associated with phonon-to-phonon collisons, and
- $l_{defects}$ = phonon mean free path associated with defects.

From Equations 2 and 3, the thermal conductivity is reduced by the decrease in the mean free path due to the introduction of material defects from irradiation, e.g., lattice defects and porosity.

For lithium aluminate at low measurement temperatures, the high concentration of stable lattice defects limit the normally-long mean free path of unirradiated materials to some uninterrupted value. Evidently,

the lattice defects in $LiAlO_2$ have saturated at a lithium burnup level less than 3.0×10^{20} capt/cm^3 (105 FPD). This is based upon by the observed, constant behavior in thermal conductivity with burnup. Continued irradiation beyond this point did not result in any further reduction in conductivity. The slight increase in thermal conductivity at 673K for the sample irradiated at 973K to 297 FPD (Figure 9) is yet unexplained. However, this sample was rerun to determine if the increase was related to experimental conditions, e.g., sample position, laser alignment, etc. However, a similar increase was again observed at the same temperature when the sample was rerun. This anomaly is not thought to be associated with swelling since very little was observed[9] in any of the the lithium aluminate samples. Preirradiation grain size for these samples was reported to be less than 1 μm and results given in Table 2 confirmed that grain growth did not occur during irradiation, even at the highest irradiation temperature.

For those samples at low burnup (105 FPD) where cool-down data were collected (Figure 10), significant increases in conductivity at low measurement temperature were observed for all irradiation temperatures. On the average, data collection at each measurement temperature took 30 - 45 minutes, providing an integrated time the sample was above a measurement temperature of 773K of about 2-3 hours. This increase in conductivity may be attributed to annealing of the irradiation defects while the samples were exposed to high measurement temperatures, thus providing a longer mean free path and relatively higher thermal conductivity. At sufficiently high temperatures, kinetic phenomena such

a defect diffusion and annihilation, and gas release allowed some degree of lattice annealing or recovery, reducing the number of phonon scattering centers resulting in increased conductivity. The thermal conductivity data from the cool-down phase represent a more characteristic 1/(AT+B) relationship. More study of the kinetic behavior of defects in $LiAlO_2$ under these conditions is necessary to quantify the observed improvement in thermal conductivity during cool-down.

5. Conclusions

An apparatus and measurement methodology were developed which allowed measurement of thermal diffusivity from radioactive ceramic materials at temperatures up to 1173K. This equipment and measurement technique minimized exposure to personnel and laboratory environments from radiological hazards (including tritium).

Sigificant decreases in thermal conductivity were observed in samples irradiated in a fast neutron environment to lithium burnups of $\leq 11.5 \times 10^{20}$ capt/cm^3. Significant reductions in thermal conductivity at low measurement temperatures were observed for lithium oxide samples as a result of radiation-induced lattice damage. The reduction ranged from 77% and 31% at 373K for samples irradiated to 4×10^{20} and 11.5×10^{20} capts/cm^3, respectively. At high measurement temperatures (1073-1173K), the thermal conductivity of all samples approached values only slightly below those of unirradiated lithium oxide. Grain growth

and swelling during irradiation were also considered and played a role in understanding the observed change in conductivity.

The thermal conductivity of irradiated lithium aluminate samples remained relatively constant with temperature at a value of about 3.5-4.0 W/m-K, for all irradiation times and temperatures. This value is only slightly lower than observed values for unirradiated $LiAlO_2$ at high measurement temperatures. After subjecting the samples to sufficiently high measurement temperatures (>650 K), an increase in low temperature thermal conductivity was observed for all aluminate samples for which measurements were made during cool-down. The low burnup sample irradiated at 1173K showed a significant improvement in conductivity reaching values comparable to observed unirradiated values.

6. Acknowlegements

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7. References

1. W. E. Gurwell, "Characterization of Commercial Alluminates, Silicates, and Zero X Materials", BNW-CC-464, January 1966, Battelle Northwest Laboratories, Richland, WA.

2. T. Takahashi and T. Kikuchi, "Porosity Dependence on Thermal Diffusivity and Thermal Conductivity of Lithium Oxide Li_2O from 200 to 900 ^{o}C", J. Nuc. Mat. 91 (1980) 93-102.

3. G. W. Hollenberg and D. E. Baker, "Thermal Properties of Lithium Ceramics for Fusion Applications", presented at the 84th Annual Meeting of the American Ceramic Society, Cincinnati, OH, May 2-5, 1982.

4. B. Rasneur, "Tritium Breeding Material: $LiAlO_2$", presented at the Sixth Topical Meeting on the Technology of Fusion Energy, March 3-7, 1985, San Fransisco, CA.

5. B. Schulz, "Thermophysical Properties of Potential Breeder Materials for Fusion Technology", presented at the International Symposium on Fusion Reactor Blanket and Fuel Cycle Technology, October 27-29, 1986, University of Tokyo, Taokai-mura, Ibaraki, Japan.

6. W. J. Parker, et. al., "Flash Method of Determining Thermal Diffusivity, Heat Capacity, and Thermal Conductivity", J. Appl. Phys. 32 (1961) 1679-1684.

7. G. W. Hollenberg, "Fast Neutron Irradiation Results on Li_2O, Li_4SiO_4, Li_2ZrO_3, and $LiAlO_2$", J. Nuc. Mat. 122&123 (1984) 896-900.

8. G. W. Hollenberg and D. L. Baldwin, "The Effect of Irradiation on Four Solid Breeder Materials", J. Nuc. Mat. 133&134 (1985) 242-245.

9. G. W. Hollenberg, "Swelling of Lithium Ceramics During Irradiation", to be published.

10. D. L. Baldwin and G. W. Hollenberg, "Measurement of Tritium and Helium in Fast Neutron Irradiated Lithium Ceramics Using High Temperature Vacuum Extraction", J. Nuc. Mat. 141-143 (1986) 305-310.

11. W. D. Turner, et. al., "HEATING 5 - An IBM 360 Heat Conduction Program", ORNL/CSD/TM-15, Oak Ridge National Laboratory, Oak Ridge, Tennessee, no date.

12. Y. S. Touloukian, et. al., Thermophysical Properties of Matter, Vol. 2, Plenum Press, New York, New York, 1970.

13. C. N. Wilson, "Fabrication of Lithium Ceramics by Hot Pressing", presented at the Annual Meeting of the American Ceramic Society, May 2-5, 1982, Cincinnati, Ohio.

14. S. W. Tam, et. al., "Saturation Phenomena and Percolative Transitions in High Temperature Thermal Conductivity of Gamma-$LiAlO_2$", J. Nuc. Mat. 133&134 (1985) 234-237.

15. G. F. Hurley and F. W. Clinard, "Thermal Diffusivity of Neutron Irradiated Ceramics", Special Purpose Materials Annual Progress Report, DOE/ET-0095, US Department of Energy (1979) 59.

FIGURE 1: Equipment for Measurement of Thermal Diffusivity of Radioactive Ceramic Materials.

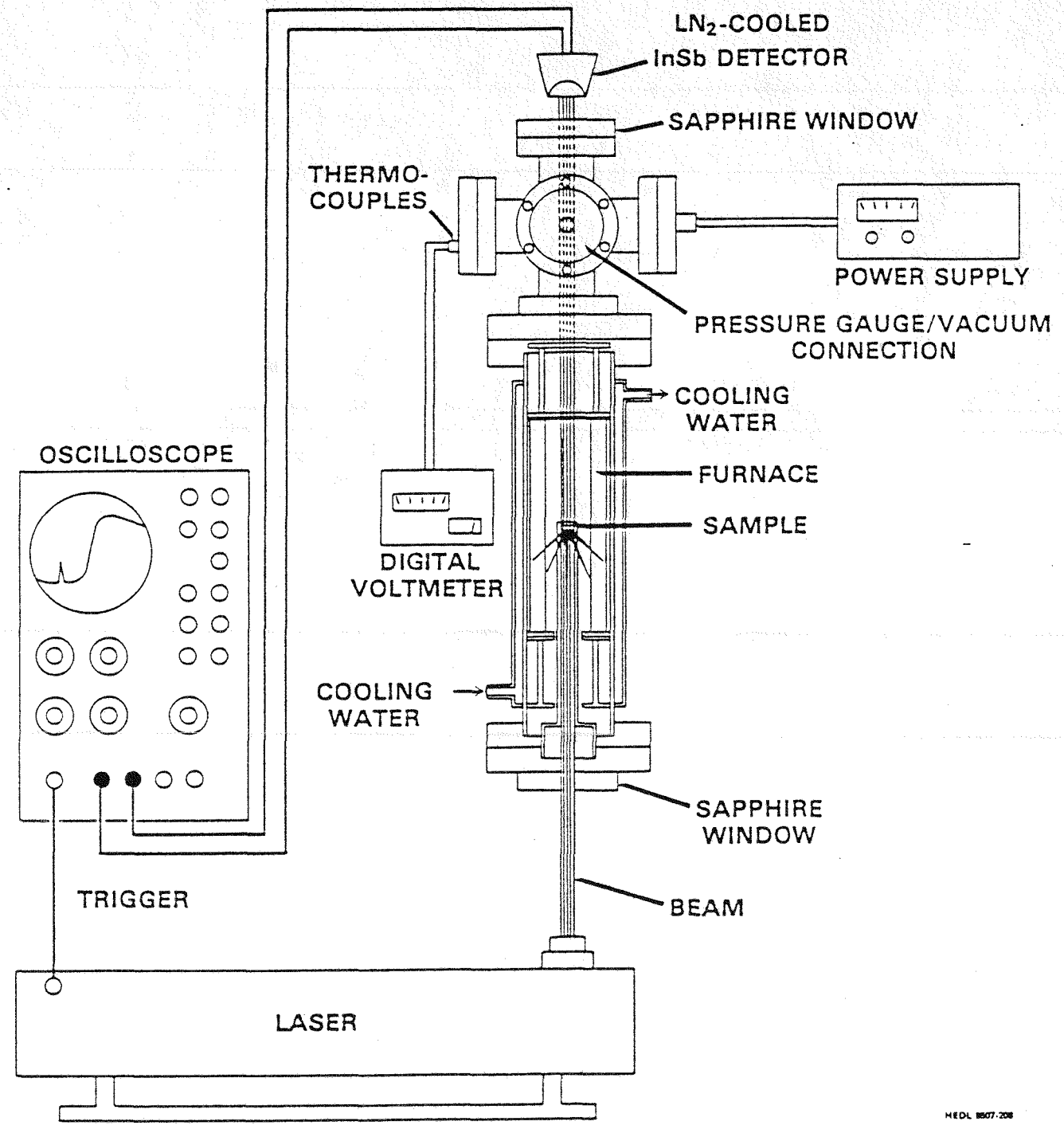

FIGURE 2: Comparison of Thermal Conductivity for Unirradiated Li_2O at 100% TD.

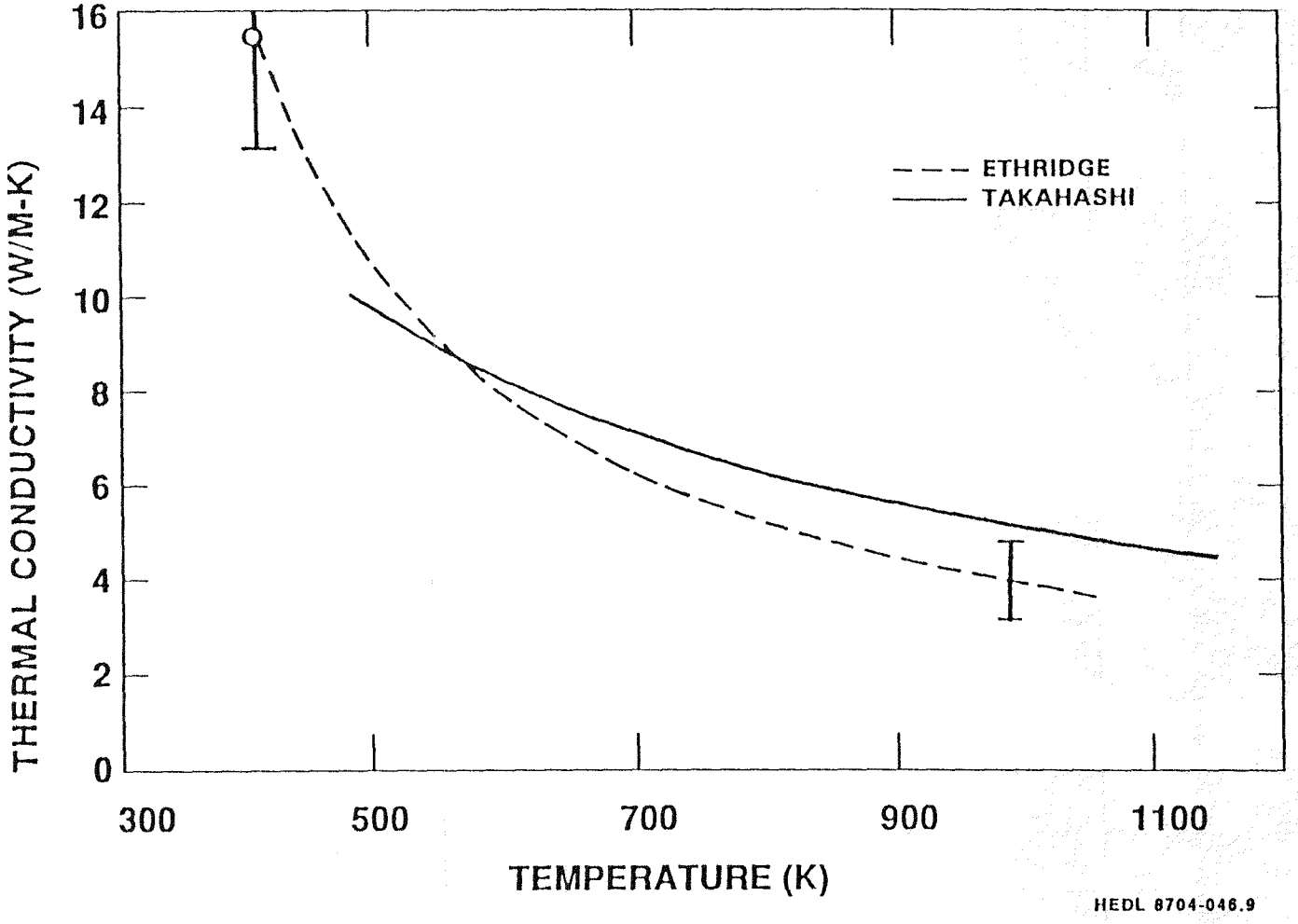

FIGURE 3: Comparison of Thermal Conductivity for Unirradiated $LiAlO_2$ at 100% TD.

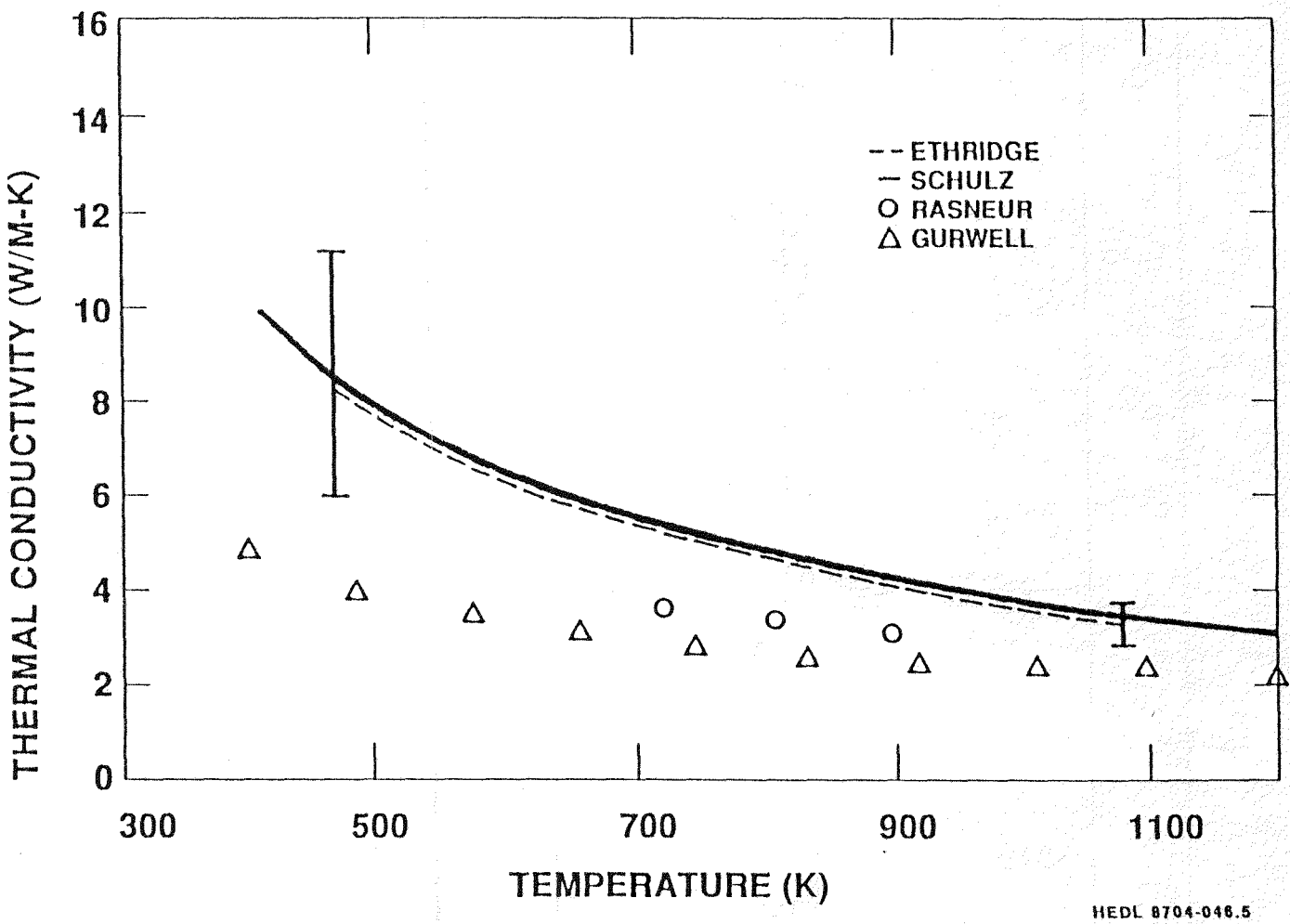

FIGURE 4: Thermal Conductivity of Li_2O at Different Irradiation Temperatures - 105 Full Power Days.

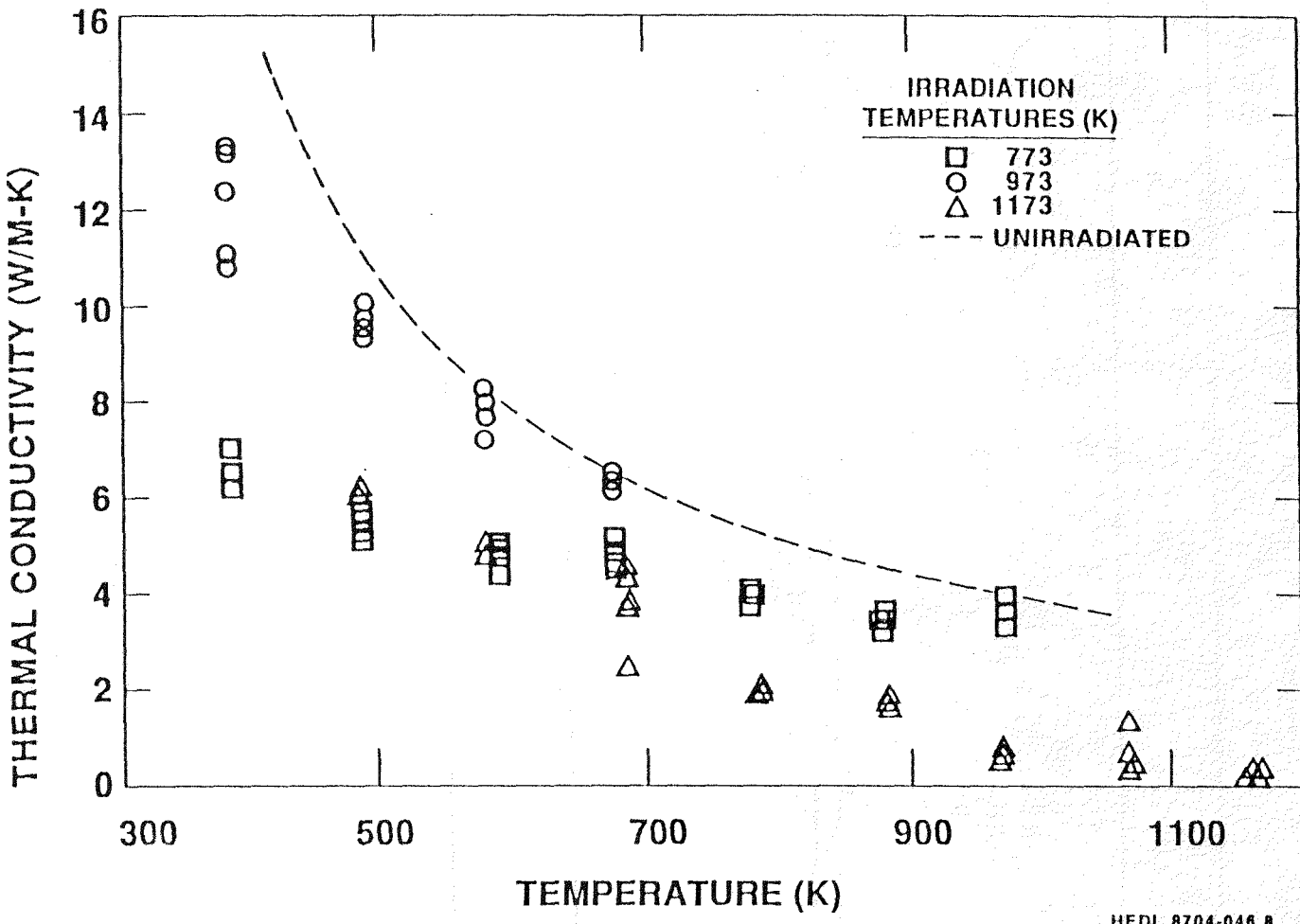

FIGURE 5: Thermal Conductivity of Li_2O at Different Irradiation Temperatures - 192 Full Power Days.

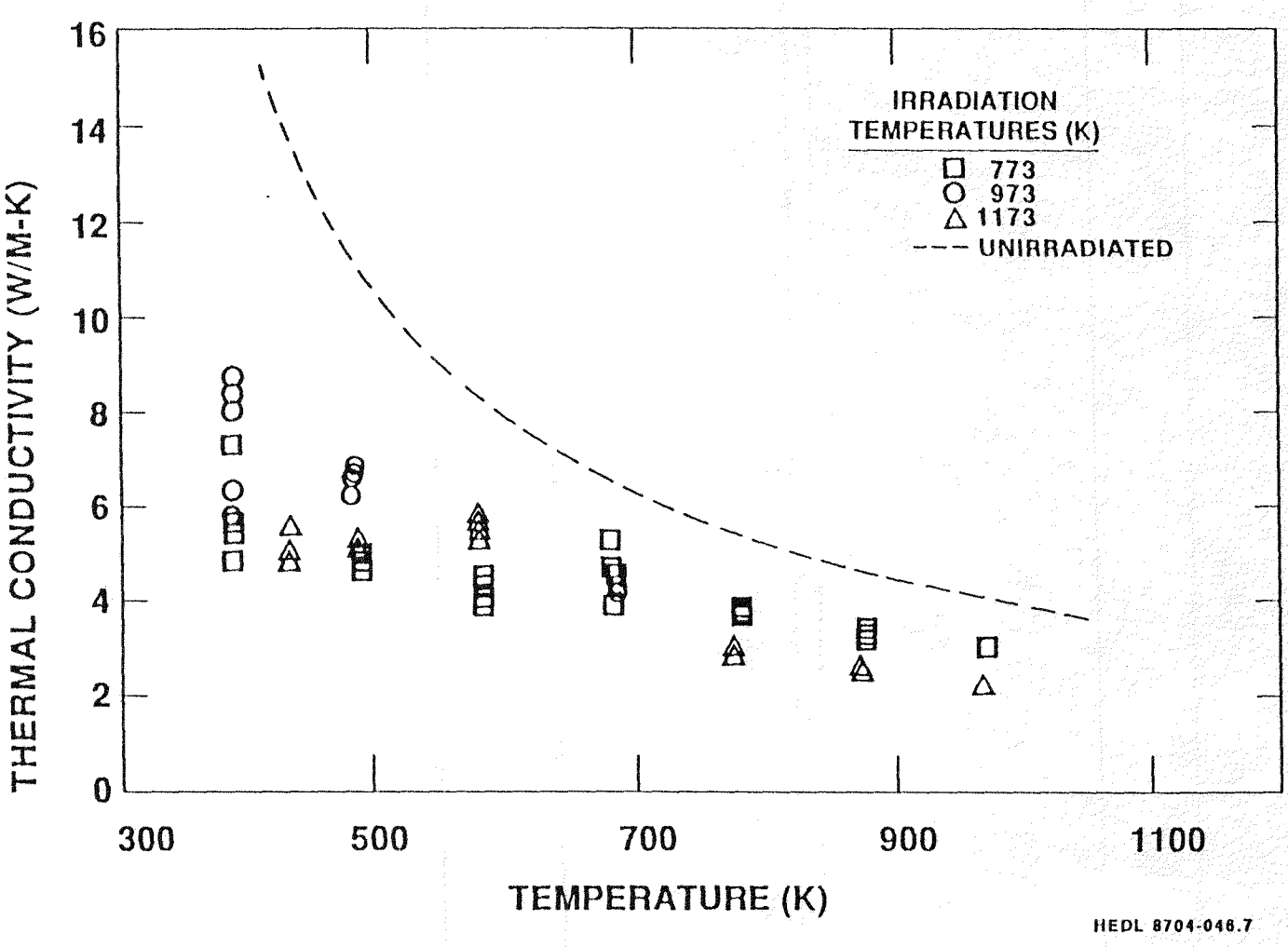

FIGURE 6: Thermal Conductivity of Li_2O at Different Irradiation Temperatures - 297 Full Power Days.

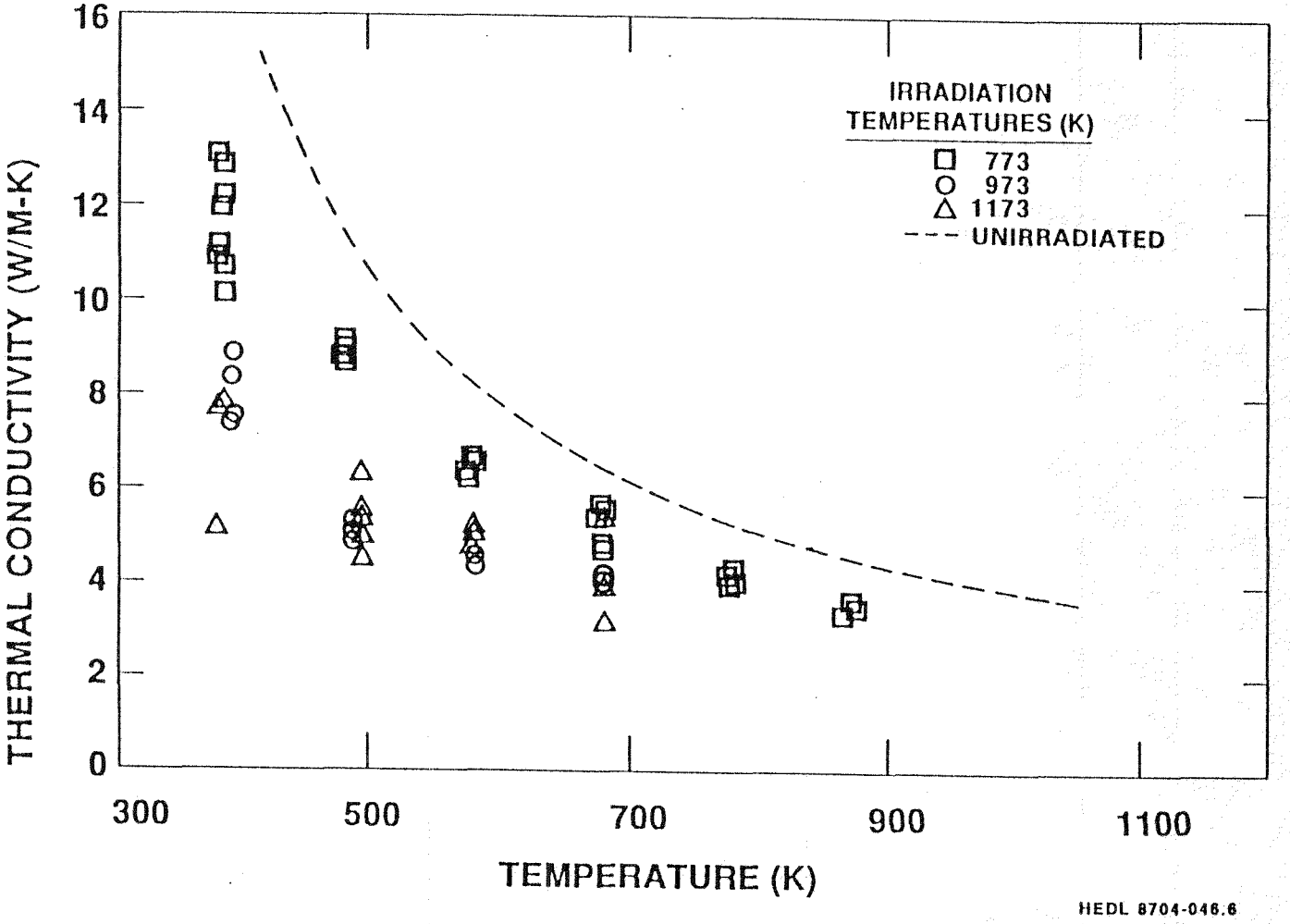

FIGURE 7: Thermal Conductivity of $LiAlO_2$ at Different Irradiation Temperatures - 105 Full Power Days (Heat-up Only).

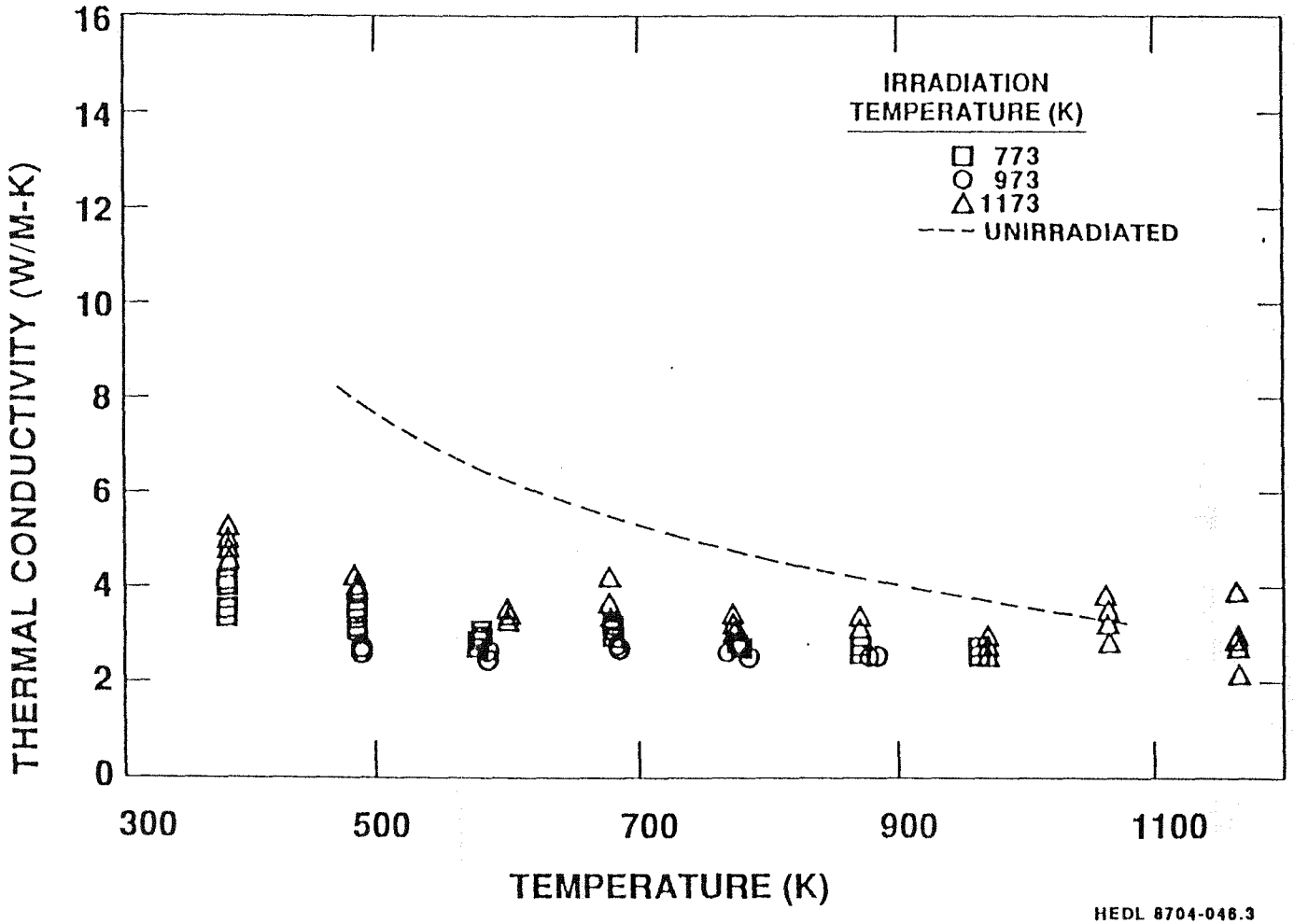

FIGURE 8: Thermal Conductivity of $LiAlO_2$ at Different Irradiation Temperatures - 192 Full Power Days (Heat-up Only).

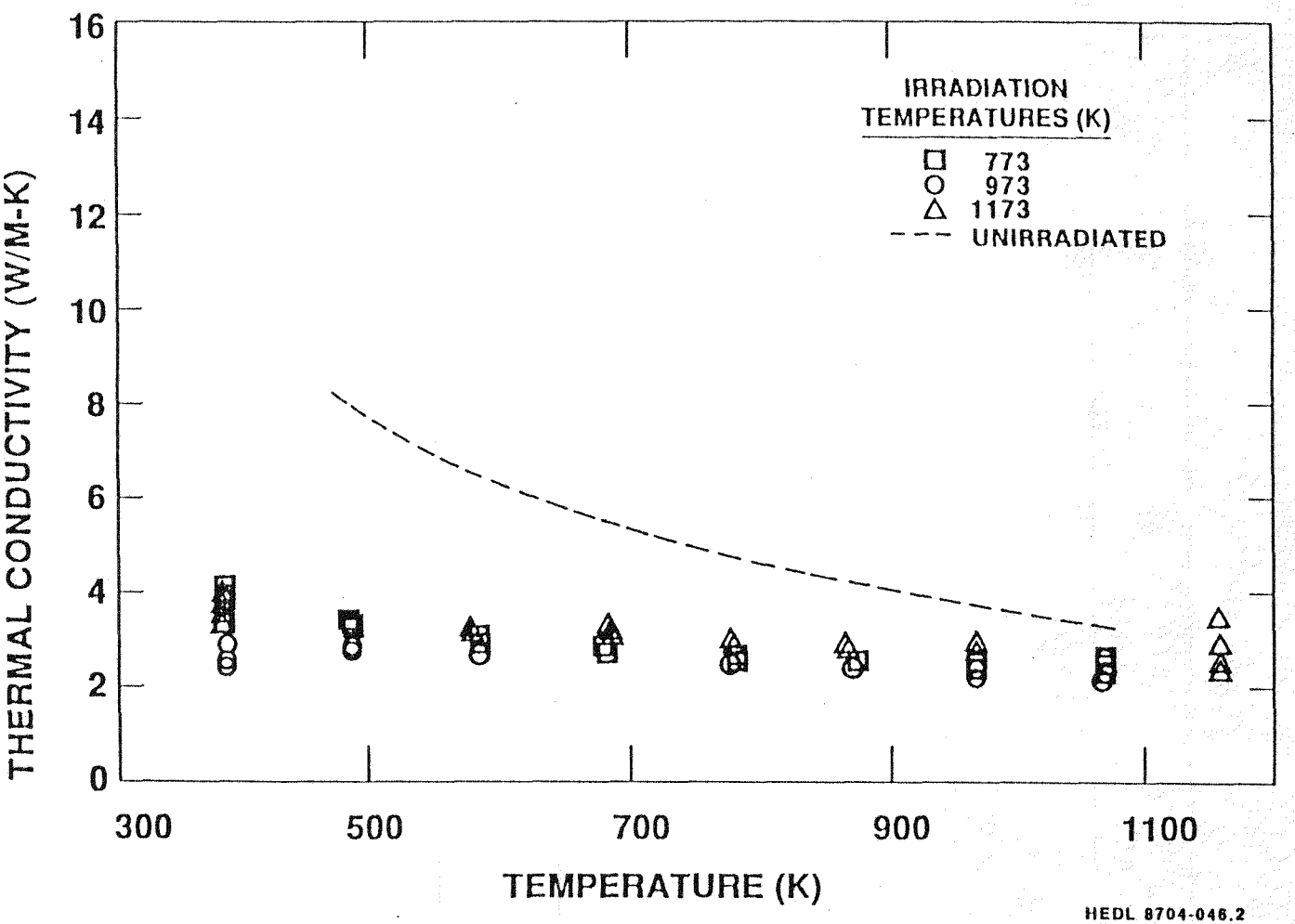

FIGURE 9: Thermal Conductivity of $LiAlO_2$ at Different Irradiation Temperatures - 297 Full Power Days (Heat-up Only).

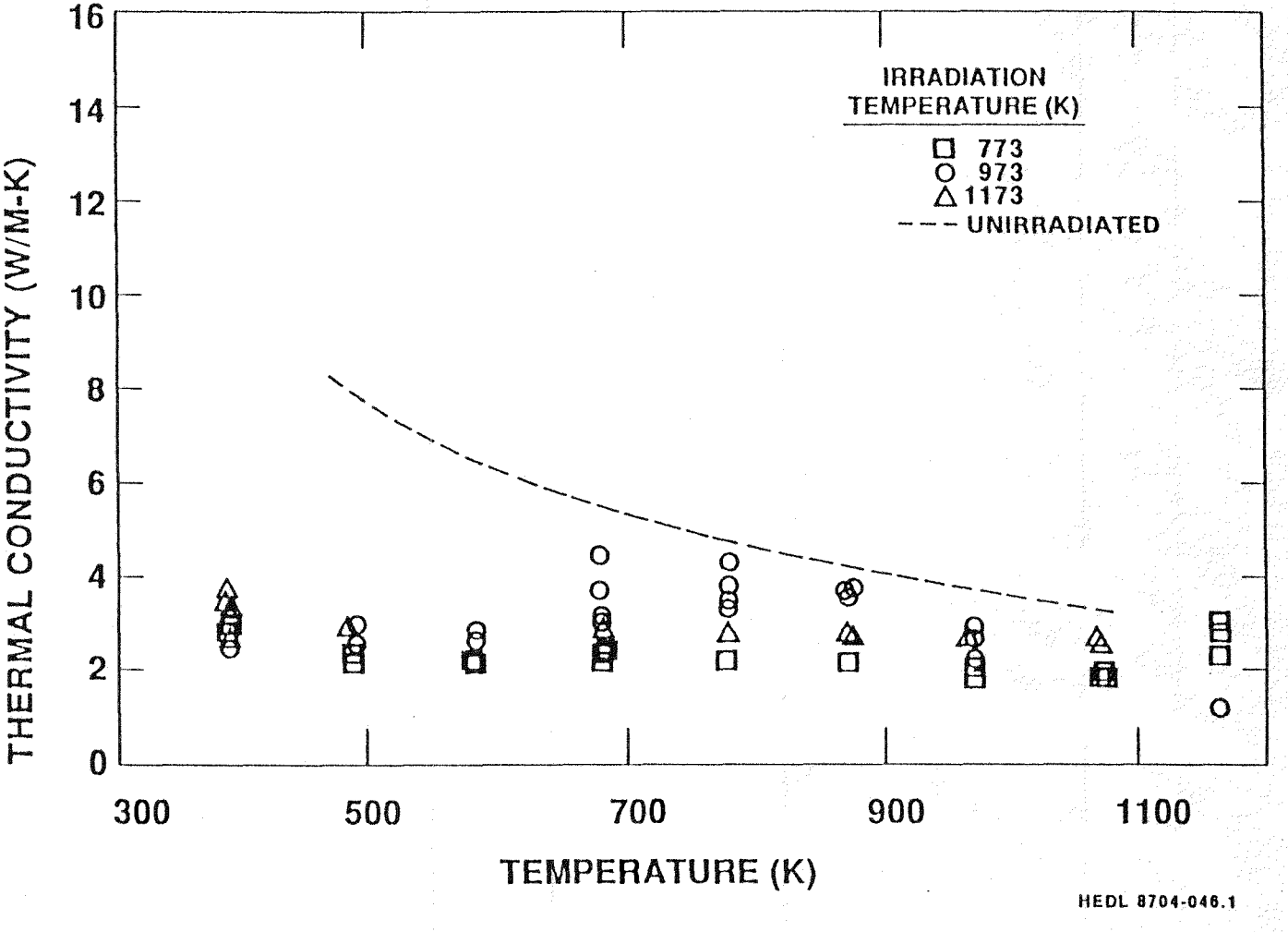

FIGURE 10: Thermal Conductivity of $LiAlO_2$ at Different Irradiation Temperatures - 105 Full Power Days (During Cool-Down).