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THE IMPORTANCE OF HYDRATION IN EXOELECTRON EMISSION FROM CERAMIC BeO*

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ABSTRACT

The influence of the state of hydration on the exoelectron emitting characteristics of BeO ceramic dosimeters for TSEE is very strong and very complex. For dosimetry the most unfavorable characteristics are a ruined TSEE peak shape and loss of intensity; this occurs if atmosphere moisture is allowed to condense onto, and evaporate from, the BeO surface. For unencapsulated dosimeters this occurs when the ambient temperature falls below the dew point. Immersion of irradiated detectors directly into liquid water for a few hours causes fading at a substantial rate, but surprisingly little change in the TSEE peak shape or intensity. The different behaviors with respect to immersion in liquid water and exposure to condensing atmospheric moisture present an enigma. Ceramic BeO TSEE dosimeters can only be used with confidence in atmospheres where below dew point conditions are avoidable, such as inside airconditioned buildings or encapsulated, dry air containers.

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INTRODUCTION

The state of hydration of the exoactive region of an exoelectron emitting radiation dosimeter such as BeO is of paramount importance in its successful operation as a radiation monitor. One school led by Krylova (1) believes that surface states involving adsorbed water or other reactive gases, are the source of nearly all exoelectron emmission. In BeO, to which this study is devoted, desiccation of the surface respectively suppresses and promotes exoelectron emission in the non-ceramic (2) and ceramic forms (3).

Unfortunately a study of the manner of adsorption and interaction of water vapor with crystalline BeO has not as yet been made. The only published surface chemical studies of BeO are those by Anderson and Horlock (4) who examined the adsorptive properties of high-area, microporous beryllium oxide and hydroxide using H_2O vapor to promote crystal growth. Like other oxides with predominantly ionic character, the surface of clean BeO should become rapidly hydroxylated upon contact with water vapor. Hydration of the subsurface layer is expected to be a much slower and more difficult process involving grain boundary diffusion.

The purpose of this contribution is to show how this latter subsurface hydration has a strong controlling effect on the sensitivity and stability of exoelectron emitting BeO ceramic. The emphasis is directed primarily towards some of the dosimetric consequences. The BeO disks were always exposed to the atmosphere prior to each TSEE reading. One can presume that the extreme outer surface was, therefore, always fully hydroxylated and that its effect on exoelectron emission was invariant.

EXPERIMENTAL

The ceramic BeO used in this study is the well-known type called Thermalox 995. It is available commercially from Brush Beryllium Co., Elmore, Ohio, USA. It can be further sensitized for exoelectron dosimetry by heating at temperatures up to 1300°C. Calibrated disks of this material, 12.5 mm ϕ, compose a reference bank of dosimeters described in ref. 5.

The reader, which has been described before (6), is of the gas-flow, Geiger counter type. It suffers from the disadvantages of a fairly low sensitivity and appreciable dead-time counting losses when radiation exposures to the BeO are above a few tens of mR. Offsetting advantages are robustness and easy exchange of BeO disks without introducing air into the counting chamber so that successive readings are possible without undue delay.

RESULTS AND DISCUSSION

The conditioning treatment of Thermalox 995 consists of prolonged sensitization (up to 500 hours) at 1320°C, cooling to room temperature and immersion in liquid water for about 100 hours (5). Drying must then be effected at a temperature which is at least as high as that experienced in subsequent readout and annealing treatments; 400°C is minimum temperature. At this point the BeO disk is in a reasonably stablized condition for TSEE dosimetry. The glow curves reproduced in Fig. 1 are for a single disk taken out of water and dried at progressively higher temperatures from 300°C to 750°C. There is an increase in intensity of TSEE and a change in peak shape. A growth occurs principally in the low temperature portions of the peak which serves to decrease the temperature for onset of TSEE by about 50°C. One deduces, therefore, that a more thorough dehydration of the subsurface,

exoactive region promotes more intense exoelectron emission and particularly in the lower temperature portions of the TSEE peak.

With more thorough dehydration, the extension of TSEE to lower temperatures is generally observed. The pathway for change in sensitivity, however, is highly individual as shown for three disks in Fig. 2. Each detector undergoes increases and decreases in sensitivity in an unpredictable manner. Furthermore, a second cycle of thorough rehydration and drying produces changes in TSEE sensitivity little related to those produced during the first cycle.

For dosimetry, some consequences of this type of behavior are less than desirable. Because no two detectors follow the same pathway for sensitization, there is no drying temperature to be chosen which can produce equal sensitivity among a group of detectors. In practice the standard deviation in intragroup sensitivity is typically about 10% (7). Also if a detector deteriorates during its working lifetime because of increased hydration, it is unlikely to be restored to its original exoelectron emitting state by heating again at the original drying temperature.

Normally we have dried detectors in the temperature range of 500°C to 600°C, which is 100°C to 200°C higher than the maximum temperature experienced during reading of the TSEE. More often than not a higher drying temperature produces an increase in TSEE which is of a transient nature. A behavior typical of a small group of detectors dried at 800°C is shown in Fig. 3. One component of the TSEE intensity decays exponentially within the hour and probably involves some moderately fast hydration event upon contact with atmospheric moisture.

Direct Immersion in Water

At the last International Symposium on Exoelectron Emission it was reported that beta emitting radionuclides in solution could be monitored by direct immersion of the Thermalox 995 disk (7). Instability problems were mentioned without going into the details.

In the interim period an interesting example of trace metal detection in aqueous solution has come to light. The BeO detector is immersed in a solution of cadmium being irradiated with thermalized neutrons. The photons from the n,γ reactions are registered by the BeO with the minimum level of detection being 10 ppm of Cd. We need to return, however, to problems of instability attending the direct immersion of BeO.

The effect that contact with distilled water has on TSEE from pre-irradiated detectors is shown in Fig. 4. Provided the time of immersion does not exceed half an hour all remains well; there is little fading and also little change in the TSEE peak shape. Soaking for longer than one hour produces fading of greater than 10%. The TL from the same BeO disk is highly resistant to fading resulting from liquid water. Immersion of the bare detector for long periods of time is, of course, necessary in the monitoring by TSEE of dissolved, low energy beta emitters at low activities. At the present stage of development it is unrealistic to anticipate widespread use of exoelectron dosimeters for solution work.

Wetting During Atmospheric Field Tests

Wetting of the BeO disk can also take place during out-of-doors exposure to the atmosphere. This occurs when the temperature falls below the dew point, an almost nightly occurence in the East Tennessee climate where all of these tests took place. Glow curves are shown in Fig. 5 for

detectors which either were, or were not, protected from condensing moisture during one such field test over a period of one week with an accumulated exposure of 15 mR. Details appear elsewhere (8). The experiences with detectors immersed directly in water lead one to anticipate fading but no deterioration in the response characteristics. Presumably the damage is due to atmospheric moisture condensing on (and perhaps evaporating from) the BeO surface for several hours at a time. The mechanism remains unknown. Why condensed atmospheric water should be so much more damaging than immersion in distilled water presents an enigma.

The deterioration is sufficient to make restoration difficult, at least by redrying at 500°C. The glow curves and integral exoelectron counts from 20 mR ^{60}Co exposure for a typically affected dosimeter are reproduced in Fig. 6. Restoration of the low temperature tail of the glow curve is particularly difficult.

One unique advantage of TSEE dosimetry is the ability to measure weakly penetrating radiations (9) (10) that are recorded with only feeble sensitivity, or not at all, by TL dosimeters. In prolonged outdoor monitoring the obvious need to encapsulate the BeO ceramic for protection against condensing moisture means loss of the capability to detect the weaker penetrating components of a mixed radiation field.

One should also be on guard against the condensation problem during normal storage in the laboratory. Excessively humid conditions can be encountered occassionally, such as during failure of the air conditioning. To prevent a condensation "catastrophe" it is advisable to store calibrated dosimeters in dry air containers. Such a catastrophe occurred with about 200 calibrated Thermalox 995 BeO dosimeters in our laboratory, the still non-distributed members of a bank of 500 dosimeters being used worldwide for research, reference, and intercomparison purposes (5).

SYNOPSIS

The problem attending dehydration and rehydration of BeO ceramic TSEE dosimeters place severe restrictions on their use. With the present state-of-the-art they must be operated in atmospheres where below dew point conditions are avoidable, such as in air conditioned buildings or dry climates. Alternately the BeO disks have to be encapsulated to exclude moisture. The dosimeters then lose the ability to detect weakly penetrating radiations such as beta rays from ^{3}H or ^{14}C, or alpha rays from ^{222}Rn and its daughters.

Three types of hydration event have been identified, in this or previous studies (3), as being able to influence the exoelectron emission from Thermalox 995. In air there is first a rapid, supposed hydroxylation of surface cleansed of atmospheric adsorbates (3). Secondly, for surface outgassed at high temperatures (such as 800^{o}C) a slower hydration event takes place during a time period of the order one hour. Usually this reduces the TSEE intensity. Thirdly, a slow hydration occurs upon exposure to liquid water in the particular form of condensed atmospheric moisture, when the emission characteristics suffer catastrophic deterioration. As a result of this latter phenomenon, many of our detectors have been more or less ruined for further dosimetry work.

FIGURE CAPTIONS

Fig. 1. TSEE glow curves, for 20 mR exposures, from a heat sensitized and liquid water hydrated BeO ceramic detector (Thermalox 995) as a function of drying at different temperatures for 30 minutes.

Fig. 2. Sensitivity changes in three detectors taken through two cycles of immersion in water, for 100 and 18 hours respectively, and denydration at elevated temperatures. Exposures standardized at 20 mR.

Fig. 3. Stabilization of response in a group of detectors dried at 800°C and exposed to air at room temperature.

Fig. 4. Fading of response, TSEE and TL, from irradiated Thermalox 995 BeO disks immersed directly in distilled water.

Fig. 5. Appearance of TSEE glow curves from two sets of three Thermalox 995 BeO dosimeters after field exposure over a period of one week; one set was maintained in a dry condition, encapsulated in thin plastic, the other set suffered wetting by condensed moisture.

Fig. 6. TSEE response of one detector to 20 mR (a) before and (b and c) after suffering moisture condensation during an out-of-doors exposure.

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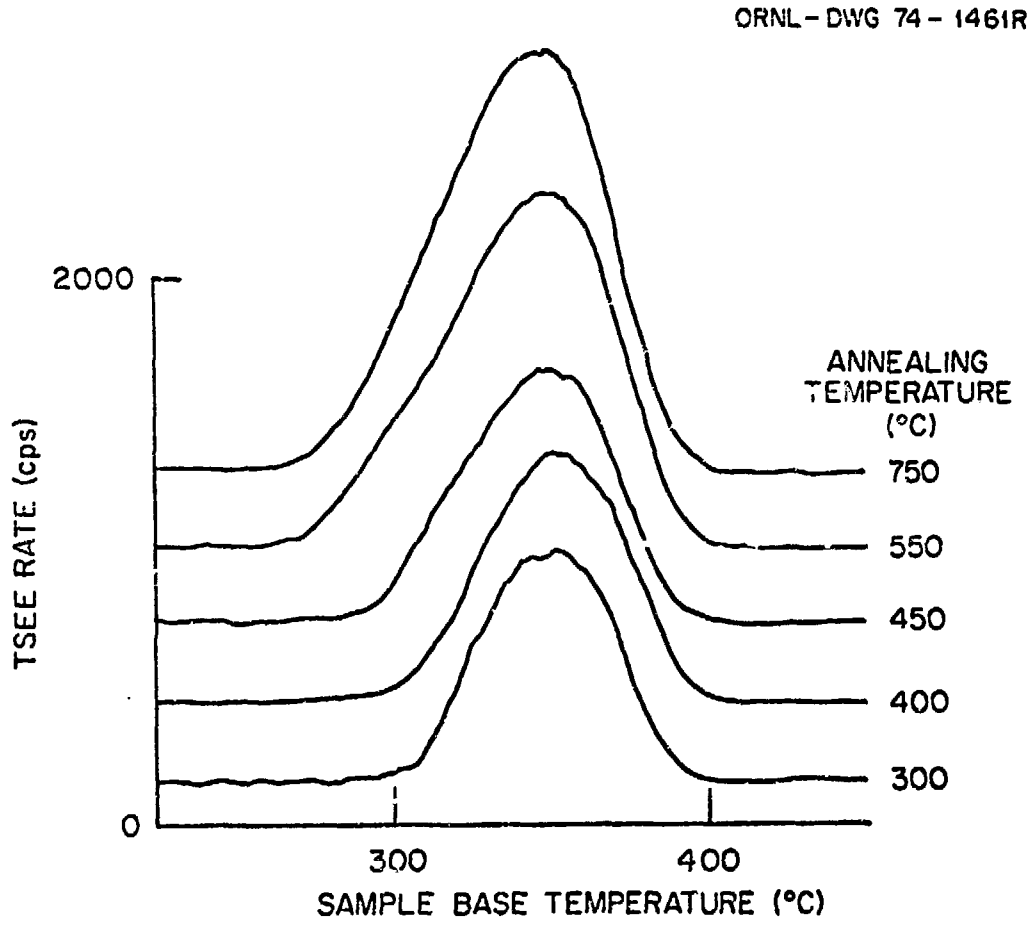
ORNL-DWG 74-1461R
2000
0
TSEE RATE (cps)
ANNEALING TEMPERATURE (°C)
750
550
450
400
300
300
400
SAMPLE BASE TEMPERATURE (°C)

Fig. 1

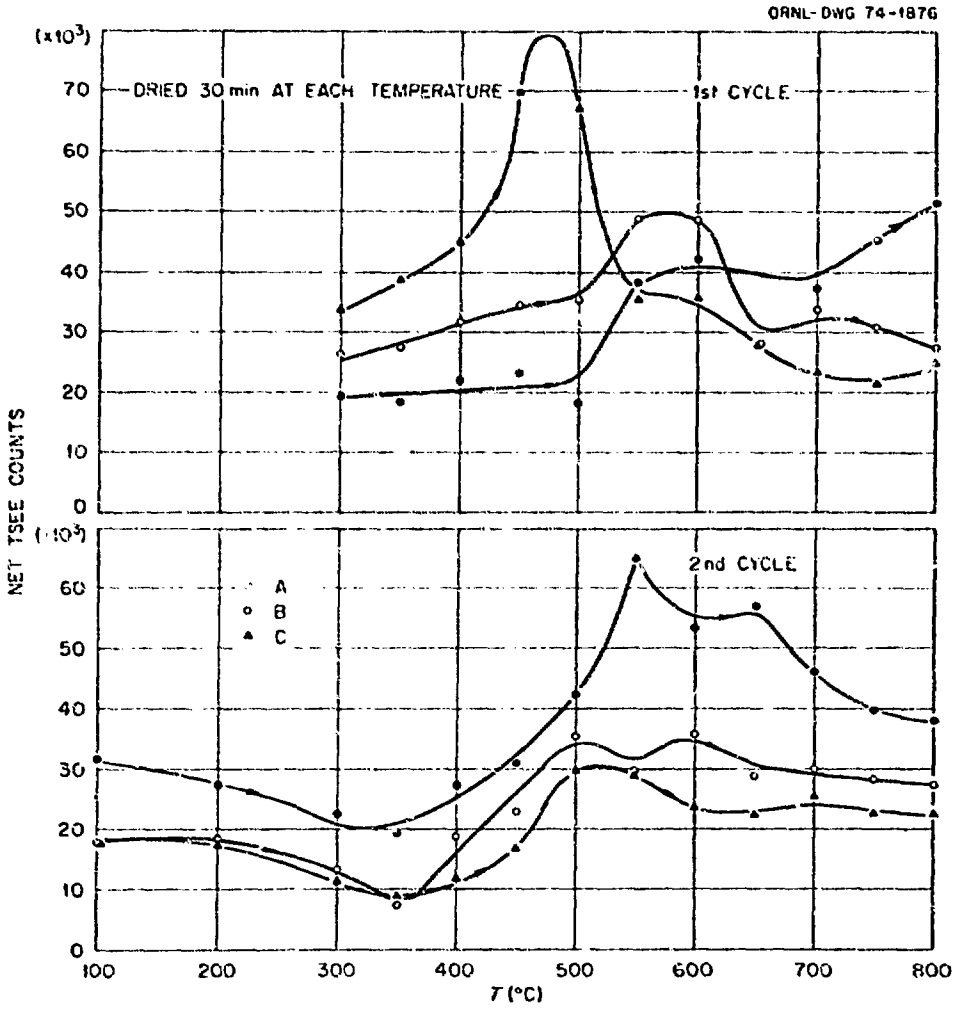
ORNL-DWG 74-1876
(x10³)
DRIED 30 min AT EACH TEMPERATURE
1st CYCLE
2nd CYCLE
A
B
C
NET TSEE COUNTS
T (°C)
0
10
20
30
40
50
60
70
100
200
300
400
500
600
700
800

Fig. 2

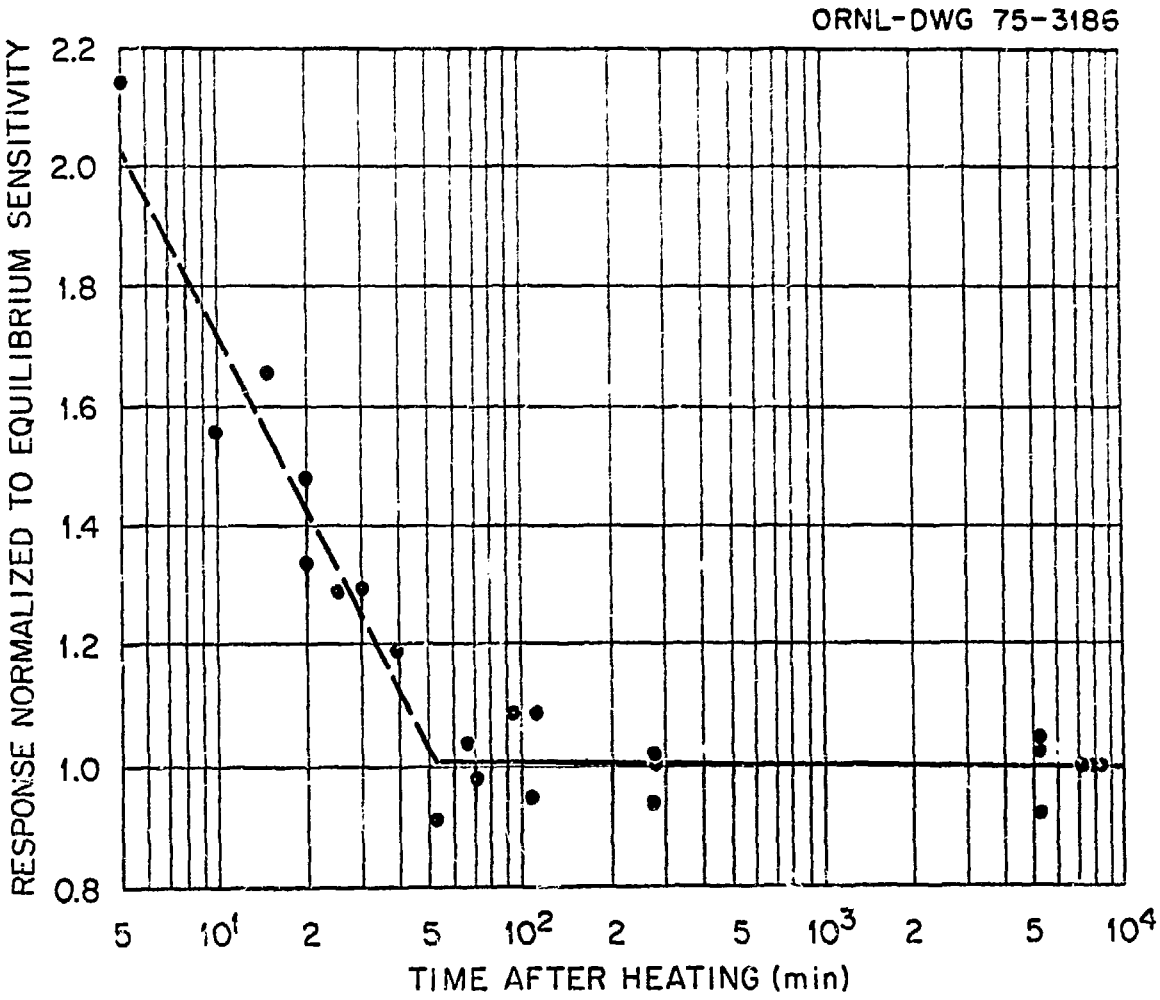
ORNL-DWG 75-3186
RESPONSE NORMALIZED TO EQUILIBRIUM SENSITIVITY
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
5
10¹
2
5
10²
2
5
10³
2
5
10⁴
TIME AFTER HEATING (min)

Fig. 3

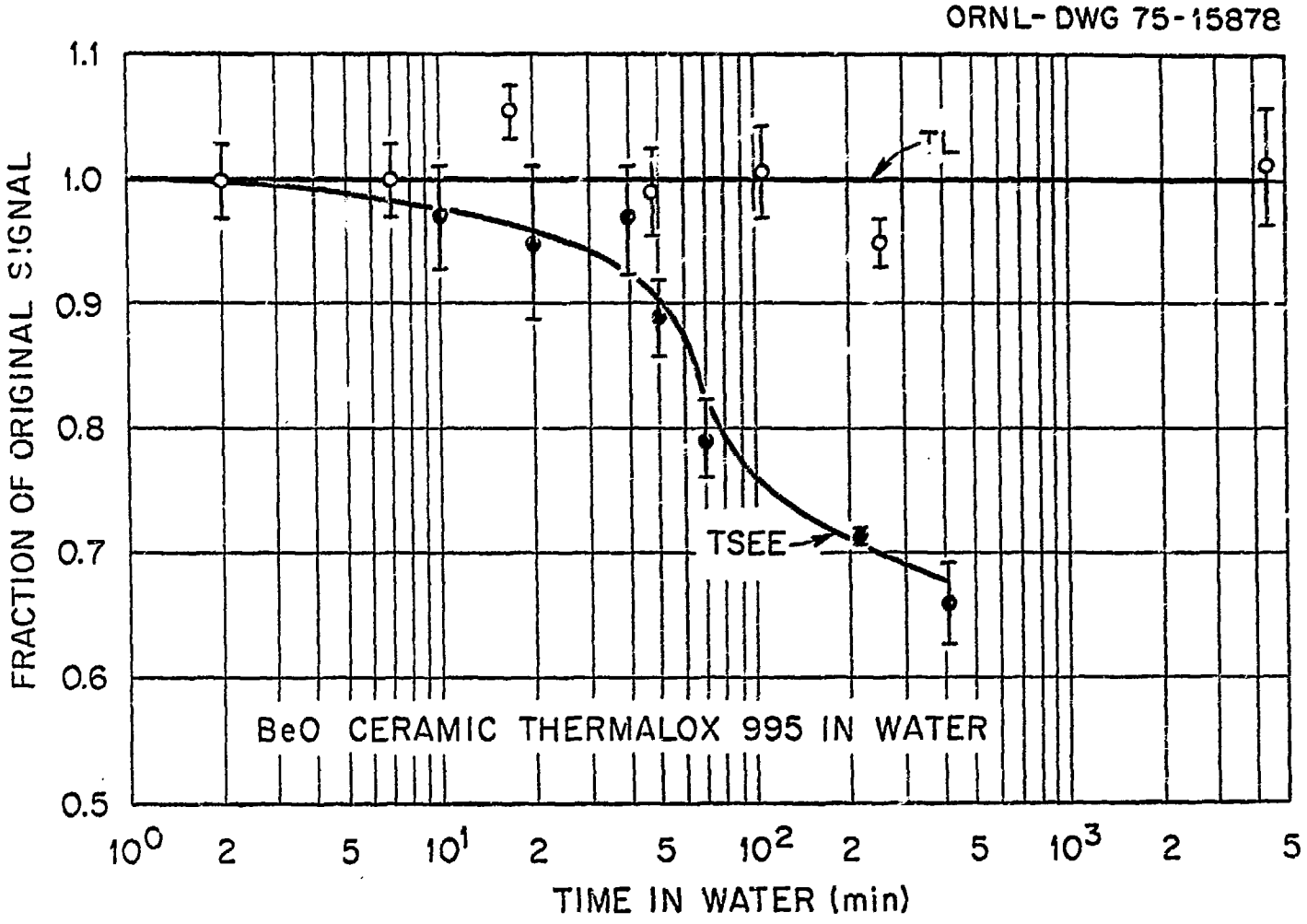
ORNL-DWG 75-15878
FRACTION OF ORIGINAL SIGNAL
1.1
1.0
0.9
0.8
0.7
0.6
0.5
TL
TSEE
BeO CERAMIC THERMALOX 995 IN WATER
10^0 2 5 10^1 2 5 10^2 2 5 10^3 2 5
TIME IN WATER (min)

Fig. 4

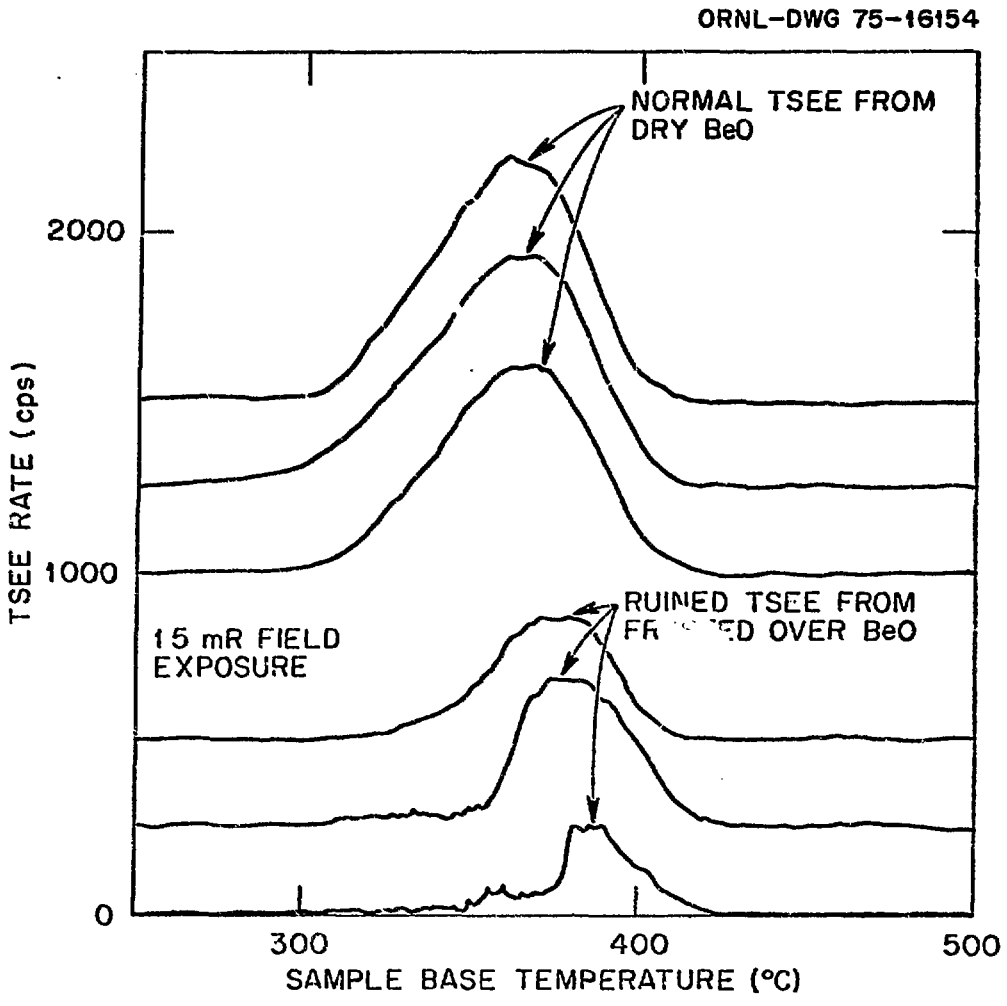
ORNL-DWG 75-16154
NORMAL TSEE FROM
DRY BeO
2000
1000
0
TSEE RATE (cps)
15 mR FIELD
EXPOSURE
RUINED TSEE FROM
FIRED OVER BeO
300
400
500
SAMPLE BASE TEMPERATURE (°C)

Fig. 5

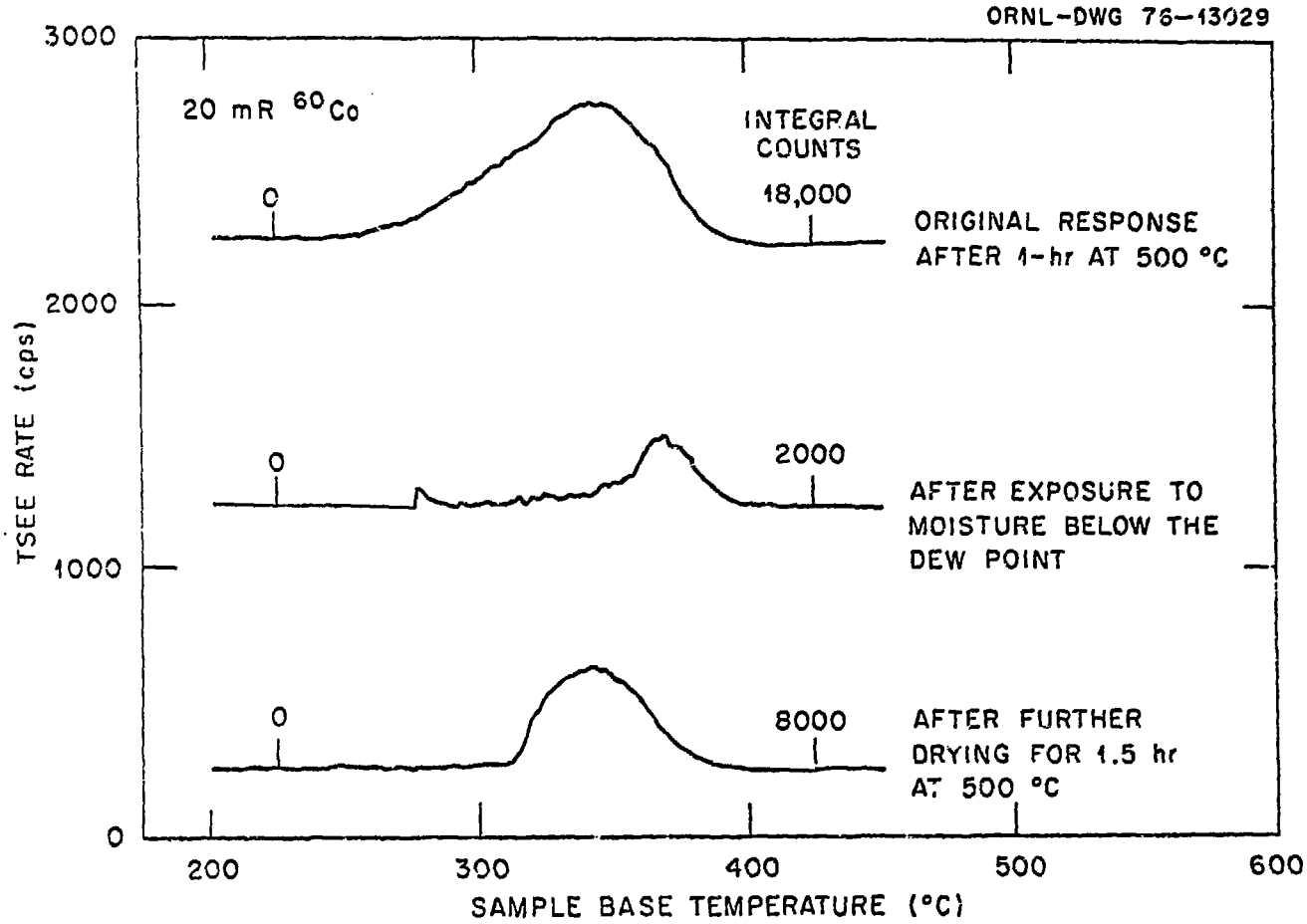
ORNL-DWG 76-13029
3000
2000
1000
0
TSEE RATE (cps)
20 mR 60Co
INTEGRAL COUNTS
0
18,000
ORIGINAL RESPONSE AFTER 1-hr AT 500 °C
0
2000
AFTER EXPOSURE TO MOISTURE BELOW THE DEW POINT
0
8000
AFTER FURTHER DRYING FOR 1.5 hr AT 500 °C
200
300
400
500
600
SAMPLE BASE TEMPERATURE (°C)

Fig. 6