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FURTHER STUDIES ON TSEE ACTIVATORS IN BeO[‡]

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ABSTRACT: In a continuing effort to study and improve the dosimetric characteristics of TSEE detectors, in particular of ceramic BeO:Si which was shown in previous studies to be a promising material, the effect of modified readout techniques and of other potential activators has been studied. In some cases, the surface was impregnated with compounds of such elements as Li, B, and Mn, prior to firing, in others the compounds (MgO, CaO, Al_2O_3) added in varying amounts prior to the fabrication of the ceramics. Also, BeO ceramics with a varying SiO_2 content have been prepared, and the properties compared to those of natural Be compounds (phenacite). The results are briefly described and discussed.

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I. INTRODUCTION

In this paper we present some results on thermal stimulated exoelectron emission (TSEE). We first give a general review of previous results, following references 1, 2 and 3.

Immediate or delayed emission of low-energy electrons (maximum energy usually 5 eV, average energy 0.2 to 0.5 eV) from thin layers (probably in most cases less than 10–100 Å) of ionic crystals (including oxidized metal surfaces) has been observed in connection with several physical and chemical processes, such as mechanical deformation, solidification of melts, changes in the crystalline structure (dehydration, uptake of crystal water), chemical reactions, and after exposure to ionizing radiation, either spontaneously or after thermal or optical stimulation. Of those sources, only the radiation-induced, optically or thermally stimulated exoelectron emission is of dosimetric interest. Only TSEE will be discussed in this paper.

Kramer[4] first drew attention to certain parallels between TSEE and thermoluminescence (TL). Experimental proof of the frequently close relation between TSEE and TL was obtained by different authors, usually by simultaneously measuring light and electron emission from an irradiated sample during heating. In particular, it was shown that in some cases the TSEE and TL maxima, as well as the fading rates of the stored information, are very similar.[5] Complete agreement between TSEE and TL is, however, rare. In a few materials, TL peaks can be observed without corresponding TSEE peaks. This may indicate that the conduction band is not involved in the TL process. In many more cases, TSEE maxima are observed without corresponding TL maxima. This is because of one or more of several possible reasons, such as electron ejection from the surface during nonradiative transfer, or to the fact that the traps from which TSEE occurs are restricted to the uppermost very thin layer of the material ("surface traps") without corresponding "volume traps" which are responsible for TL emission.

Despite some remaining difficulties in the interpretation of results, it seems that the obvious similarities of thermoluminescence and TSEE indicate a similar basic mechanism. Assuming deep acceptor (electron) traps, deep donors and a sufficient gap between conduction band (normally empty) and valence band, ionizing radiation lifts electrons from the valence into the conduction band (ionization), or causes the "injection" of electrons liberated in the environment into the crystal. They are fixed in electron traps, thus preventing combination with holes.

If sufficient thermal or optical energy is transferred to the system (stimulation), three effects will, in principle, be observed simultaneously, the characteristic peak temperature being an indicator of the depth of the electron traps:

1. electrical conductivity proportional to the electron concentration in the conduction band;
2. electron transfer from the conduction band to deep activators associated with photon emission (TL glow-curve) ; and
3. electrons leaving the surface with a probability which depends on temperature, work function, and surface structure. It is not completely understood whether electron ejection occurs as some sort of non-stationary glow-emission from the conduction band (with the high-energy tail of the electron energy distribution overcoming the work function), or if other direct emission mechanisms are dominating (for a more detailed discussion, see Ref. 3).

Of course, this model is oversimplified. For example, there is usually not a well-defined single trap depth but a trap-depth distribution, as evidenced by the dose dependence of the peak location, which indicates a preferential filling of deeper traps at lower dose levels.[11]

Numerous parameters have been shown to affect the surface electron trap density and distribution and, consequently, qualitatively and/or quantitatively the TSEE emission characteristics of a given chemical compound. Only a few can be mentioned here:

1. Both sensitivity and peak height distribution depend on the ionization density (LET) of the radiation, resulting in substantial differences between, for example, alpha and gamma irradiation effects in some materials.[6]
2. Heat pretreatment has for a long time been known to sensitize or desensitize materials such as $CaSO_4$, LiF, and CaF_2. Recently, an optimized sensitization of ceramic BeO, which is a particularly interesting material for TSEE dosimetry, has been observed.[7] It should be noted that this sensitization is frequently reversible due to the uptake of H_2O or other reactions at the surface.
3. Pre-exposure of materials to heavy charged particles, x-radiation, or gas discharges has been found to increase TSEE sensitivity in some cases and frequently changes the "glow-spectrum" (F and M centers frequently act as electron donors in TSEE).
4. It appears that the role of activators in TSEE is rather complex. A number of investigators found a pronounced effect of different activators in materials such as NaCl, CaF_2, $CaSO_4$, ZnO, and

ZnS. Preliminary studies with LiF and BeO from various sources[8] did not lead to conclusive results. Only recently, the presence of SiO_2 in the emitting surface was shown to be closely related to the main TSEE peak in ceramic BeO.[9]

Basic criteria for selection of a material suitable for TSEE dosimetry are:

1. TSEE should not occur below approximately 150 °C because the thermal fading rate at room or slightly elevated temperatures would be too rapid. However, TSEE should not occur at very high temperatures because it is difficult to measure TSEE peaks above approximately 600-700 °C due to the rapidly increasing thermionic electron emission in this temperature range.
2. If the materials are not used exclusively in sealed dosimeters, they should be chemically and thermally stable enough to withstand many heating cycles (annealing, reading) in air and in counting gases without changes of their dosimetric properties.
3. The material should be sensitive, i.e. emit a large number of exoelectrons per unit surface area per unit radiation dose.
4. The dosimetric properties such as LET dependence, linearity of response, etc., should be optimal for the particular application.

Of all the materials studied so far, a commercial ceramic BeO (Brush Thermalox 995) fulfills these criteria best. It exhibits little or no toxicity, thermal and mechanical stability, and can be easily obtained in rather inexpensive disks or rods of varying size.[10] Therefore, the studies described in this report have been restricted to this material. It has been the goal of these experiments to further improve the evaluation techniques; and to investigate the effect of activators other than SiO_2 and of radiation damage on the sensitivity. The study is a continuation of the efforts of the ORNL team to optimize the properties of TSEE dosimeters, which have been recently summarized on another report.[11]

II. INSTRUMENTATION

The gas-flow GM counter which was previously used for TSEE studies at ORNL,[12] employing a linear temperature controller,[13] has been modified as follows:

a. The counter was used in the proportional region. A flow of 10% methane and 90% argon was used as a counting gas. With a ^{170}Tl source, a plateau with a 200 volt length and a 3% slope was established. An operational voltage of 2325–2375 volts gave the most satisfactory and reproducible results for TSEE measurements. Counter dead time corrections can be made, considering the $10\,\mu$sec pulses from the main amplifier.

b. A channel analyzer to be operated in the multiscaler or pulse analyzer mode has been incorporated into the counting system. A block diagram of the circuitry employed is given in Fig. 1. An amplification factor of 500 is used and a proper discrimination level is chosen at the single channel analyzer to cut off the noise signal from the detector and amplification stages.

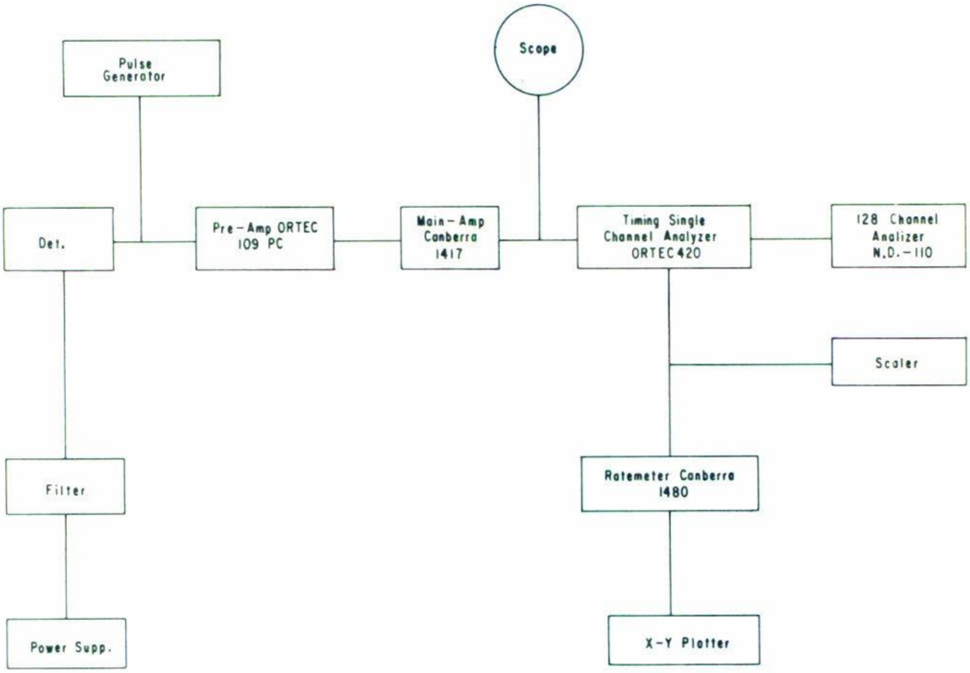

Fig. 1. Block diagram of TSEE counting system as used in part of the experiments.

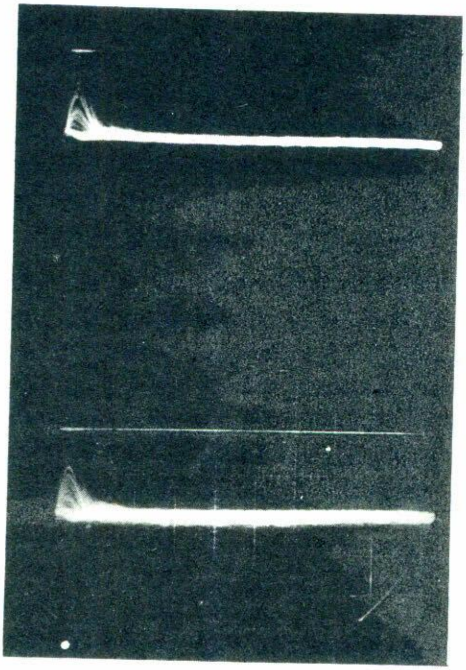

Fig. 2. Typical TSEE avalanche as obtained with the proportional counter (5 V/cm, 10 μsec/cm).

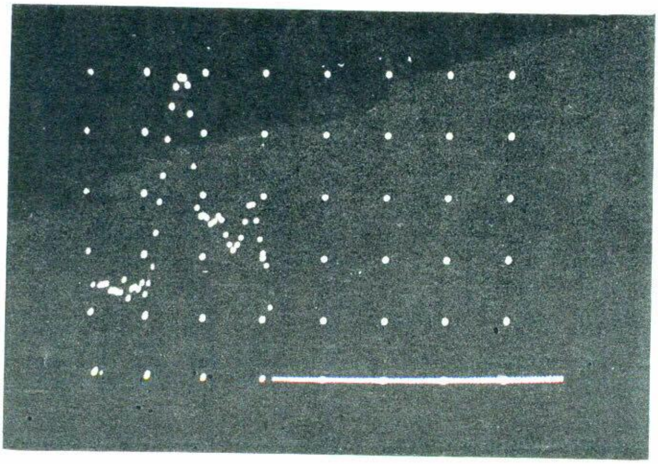

Fig. 3. TSEE curve of ceramic BeO (Thermalox 995), with channel analyzer operated in multiscaler mode (10 sec/channel, 2°C/sec).

The advantages of these changes are an apparent sensitivity increase for any given detector by a factor of ~8 because of a higher efficiency of exoelectron registration; and an improved resolution of multipeak spectra as compared to the X-Y plotter. A typical TSEE avalanche from the proportional counter is presented in Fig. 2. In Fig. 3, the TSEE curve (emission rate as a function of temperature) of ceramic BeO: Si (Thermalox 995) is given. The three peaks at ~325 °C, ~450 °C, and ~550 °C can easily be distinguished.

III. ACTIVATION BY DIFFUSION

Both lithium[14] and boron[15] are known to enter the BeO lattice, solid solution of boron occurring up to ~0.25 percent.[16] In Thermalox 995, however, only 2 ppm of each impurity can be detected. Attempts have, therefore, been made to activate the surface of BeO 995 with Li and B in the hope of favorably modifying the TSEE characteristics. A profound difference exists between the substitutional cations, boron being a site of electron deficiency, lithium one of electron excess. Therefore, their TSEE activation potentials should differ markedly. Two factors complicate, however, the reproducibility and quantitative interpretation of results. One arises from the fact that at the high temperatures required to diffuse Li_2O or B_2O_3 into the BeO, those compounds tend to evaporate. Furthermore, they may affect the TSEE indirectly by changing the surface conductivity, work function, etc.

A saturated solution of boron oxide was used for impregnation of the BeO. No significant changes in the TSEE spectrum could be induced for any temperature up to 1400 °C (melting point of B_2O_3 460 °C) other than a slight overall depression of the exoelectron emission.

The initial lithium doping experiments were attempted by diffusing Li_2O into the surface of BeO at 1200° or 1400 °C. High temperatures were chosen because the reported melting point of Li_2O is > 1700 °C. It was later learned[17] that Li_2O and BeO form a compound of suspected composition Li_2BeO_2 whose thermal stability is very poor above its melting point (which is only known to be less than 950 °C). Furthermore, virtually all of the lithium can be removed by sublimation if prolonged heating is carried out between 1000° and 1500 °C.[17] Experiments designed to activate BeO with Li_2O were subsequently made in a temperature range of 650–1100 °C.

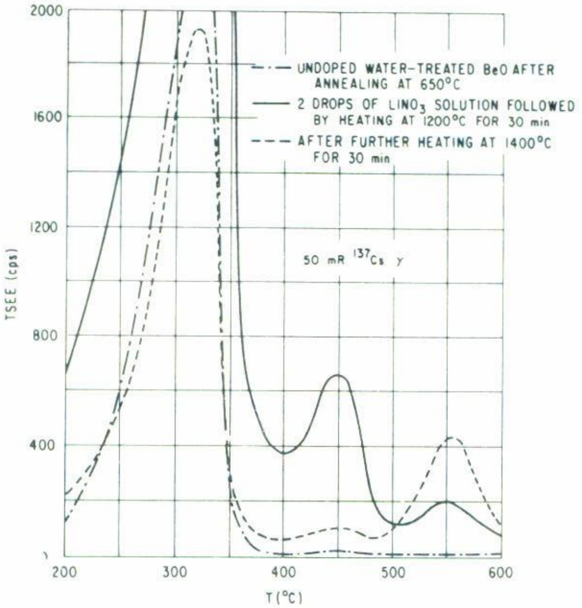

Fig. 4. Changes in the TSEE curve of ceramic BeO (Thermalox 995) after treatment with lithium (two drops contain approx. 10 mg $LiNO_3$) at 1200 °C, and at 1400 °C.

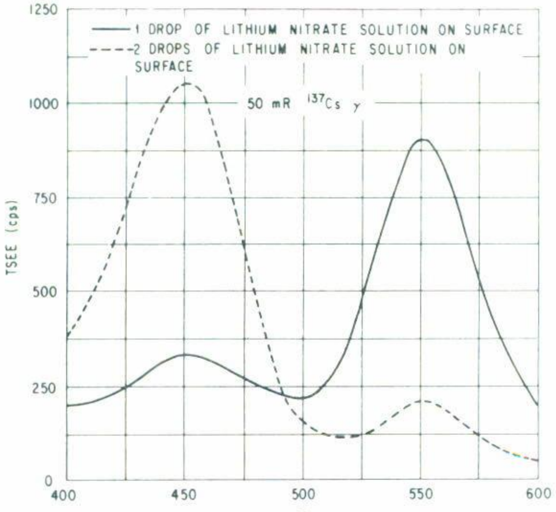

Fig. 5. Effect of different amounts of lithium on the high temperature peaks in ceramic BeO after heating to 1200 °C.

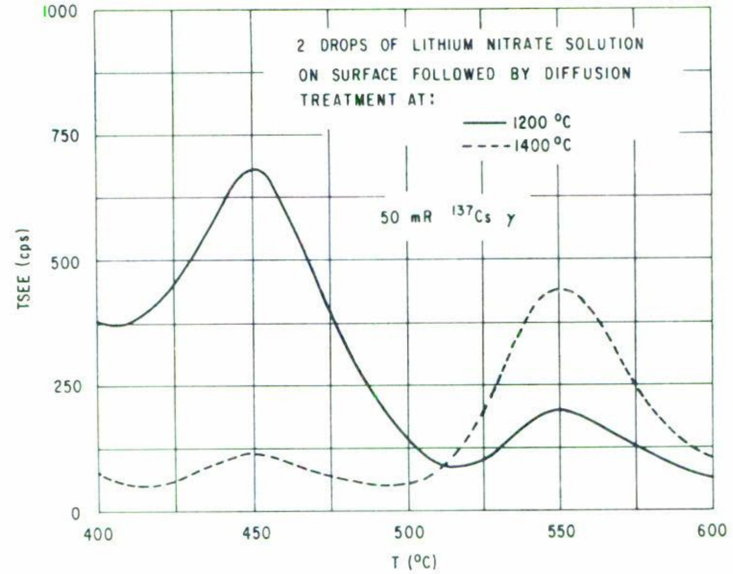

Fig. 6. Effect of heating temperature on the high-temperature peak ratio in ceramic BeO.

As can be seen in Fig. 4, lithium activation enhances the high temperature peak (∼450° and ∼550°C) intensities compared to a "blank" BeO dosimeter whose surface had been wetted with water instead of $LiNO_3$ solution. The prominent peak at ∼325°C is much enhanced by lithium doping after the 1200°C treatment but its intensity falls as the lithium is removed at 1400°C. The relative enhancement of the two high temperature peaks seem to depend on the amount of dopant added (Fig. 5). After wetting the surface of a Thermalox 995 disk (diameter 25 mm) with one drop of a 10% $LiNO_3$ solution in water (∼5 mg $LiNO_3$) and thermal treatment at 1200°C, the ∼550°C peak predominates over the ∼450°C peak and vice versa for twice the amount of $LiNO_3$ or more. The diffusion temperature is also of importance; Fig. 6 demonstrates that after ∼10 mg of $LiNO_3$ are added, increasing the temperature from 1200° to 1400°C switches the ratio of peak intensities. Since Li_2O is being sublimed more rapidly at 1400°C, perhaps raising the temperature by 200°C has the same effect as reducing the quantity of lithium, that is promoting the intensity of the ∼550°C peak over the one at ∼450°C. These results indicate that two kinds of trapping centers are being introduced, their relative concentrations and/or ability to emit exoelectrons depending on the amount of lithium present.

For the activation carried out below 1200°C, the disks were fired after $LiNO_3$ impregnation for one hour at different temperatures. As can be seen in Fig. 7, activation begins at about 800 °C, maximizing close to 1000 °C when the intensities of the TSEE peaks at ~450° and ~550 °C are increased by 50 and 20 fold respectively. It is tempting to asociate the enhanced exoelectron activity with the formation of "Li_2BeO_2", its instability above 1000 °C accounting for a reduction in activity (a similar behaviour has been observed with silicon activation, where compound formation of phenacite Be_2SiO_4 at 1400 °C coincides with a high exoelectron activity at 325 °C.[9]) The lithium can also interact with the Be_2SiO_4 as evidenced by the changes in the intensity of the exoelectron emission at ~325 °C.

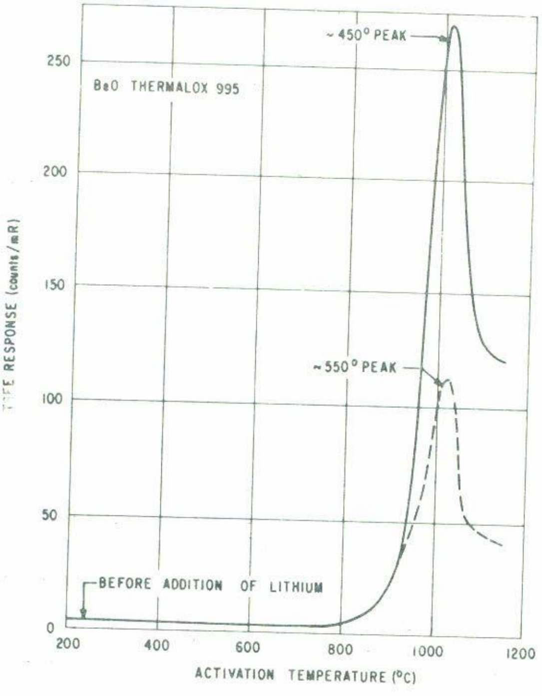

Fig. 7. "Activation" of the high-temperature peaks in ceramic BeO by surface treatment with Li as a function of heating temperature.

Substitutional Li^+ in BeO probably serves as a hole trap not contributing directly to the exoelectron emission process. The substitution, however, should be accompanied by oxygen vacancy formation in order to preserve charge neutrality. These electron deficient defects are potential electron traps (F^+ centers) which might be acting as exoelectron emitters at high temperatures. Heavy particle irradiation, for instance with α particles, may create oxygen vacancies, in addition to other types of damage

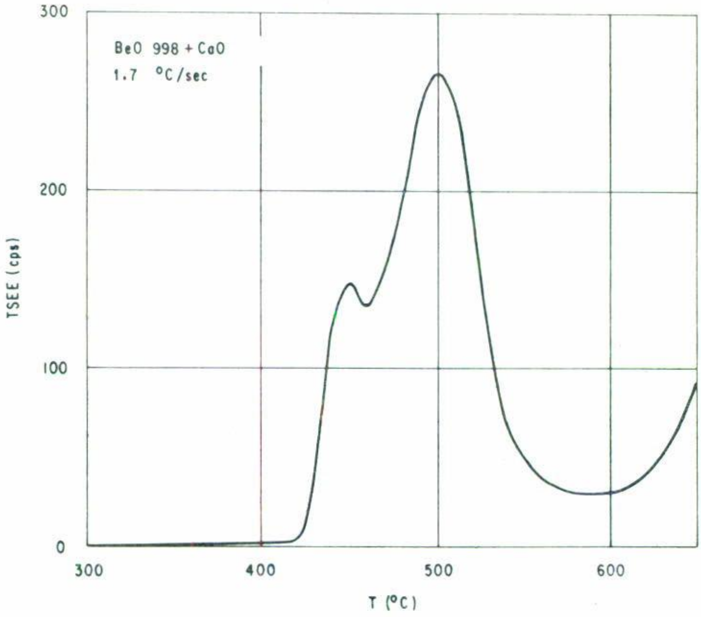

Fig. 8. TSEE of ceramic BeO (Thermalox 995) after impregnating the surface with a $Ca(OH)_2$ solution and heating for two hours at 1200°C.

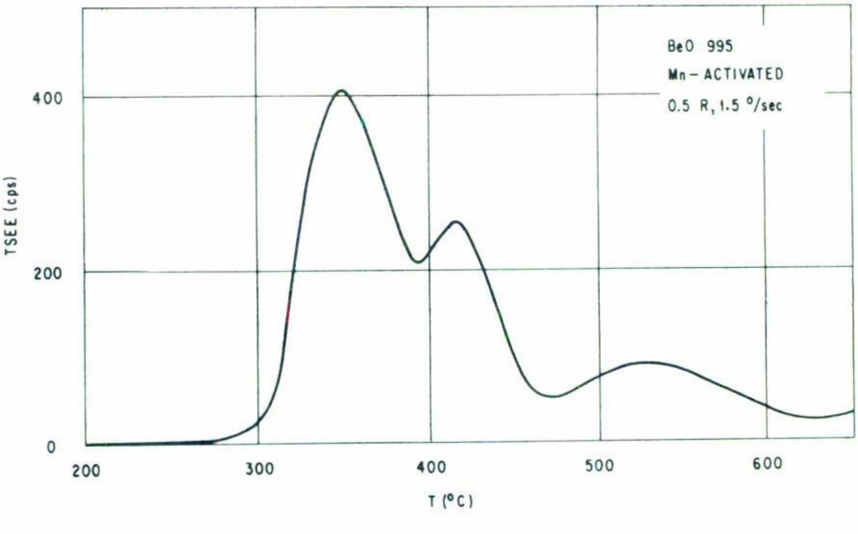

Fig. 9. TSEE of ceramic BeO after impregnation of surface with $MnCl_2$ solution and heating for 2 hours at 1200°C.

centers. The fact, therefore, that both lithium doping and preirradiation of the detectors with α particles enhance the emission at 550 °C[9] suggests an emission from oxygen vacancy traps. The F^+ center in neutron irradiated single crystal BeO has been characterized fully.[18]

Unfortunately, the response of lithium activated BeO is somewhat erratic which makes it unlikely that $BeO \cdot Li_2O$ has practical value for dosimetry. Perhaps the lithium imparts hydrophilic character to the surface because of its higly polar nature and this makes the surface doped BeO more prone to chemical attack by atmospheric constituents, resulting in instability. Particle irradiation was found to produce similar but more stable and reproducible effects.[11] Recently, the results of similar studies[19] came to our attention, in which liquid lithium metal was used for the doping. Again, maximum sensitization was reported to occur around 1000 °C.

Stable coordination occurs with the acidic oxides of small cationic radius and high cationic charge to form the beryllium salt of a complex oxygen-containing anion. Hence doping was attempted with phosphorus pentoxide as phosphoric acid, an acid which dissolves BeO. Phosphorus pentoxide when deposited on the BeO surface, eliminated all TSEE signals. Not until the diffusion temperature had been increased to 1400 °C did the ~325 °C peak return as the phosphorus distilled out. No new TSEE peaks were seen.

A remarkable change in the TSEE curve was observed in samples of a rather pure ceramic BeO with low Si content (Thermalox 998) after it has been heated to 1400 °C with a $Ca(OH)_2$ layer at its surface (Fig. 8). Without CaO, this material is very insensitive and exhibits a peculiar "self-excitation" (increasing signal during consecutive heating cycles without irradiation). After CaO, treatment, the self-excitation effect disappears and peaks at ~450 and 500 °C are observed. It can be speculated that the disappearance of self-excitation is related to a change of the surface conductivity. Conductivity measurements are planned.

"Activation" has also been attempted with some heavier cations which have been used previously in other crystals as TL or TSEE activators. Some of them such as Ti did not produce, after heating of the impregnated surface at ~1400 °C, any substantial effects in the TSEE characteristics, while others such as Mn (Fig. 9) clearly modified the TSEE curve by the creation of new peaks or changing of the peak ratio. A dramatic sensitivity increase was, however, not noticed with any of these treatments.

IV. ADDITION OF OTHER OXIDES

It has been found earlier[9, 11] that SiO_2, probably in part as phenacite (Be_2SiO_4), appears to be responsible for the pronounced main peak at ~325 °C* in ceramic BeO (Thermalox 995). The bulk concentration of SiO_2 in this material is about 0.2%, but it is enriched in the surface to about 1%. The SiO_2 is, however, not distributed homogeneously over the surface, but further concentrated probably at grain boundaries. The degree of enrichment depends strongly on the manufacturing procedure. It also is difficult to determine the actual SiO_2 concentration at the exact locations from where TSEE occurs at the surface of the ceramics (probably mostly from highly disturbed regions such as grain boundaries and growth steps). Therefore, it is presently not possible to precisely determine the correlation between SiO_2 concentration and TSEE response.

Experiments with sintered mixtures of BeO and SiO_2 of varying composition have been carried out. Despite the limitations in the interpretation of the results, it appears that an increase of the SiO_2 content leads to a further increase in the sensitivity, perhaps up to a composition corresponding to phenacite. Also multiple recycling (one hour at 1500 °C, followed by one hour at 1400 °C) tends to increase the sensitivity of Thermalox 995. This could be explained by an increase in the surface concentration of SiO_2. However, natural phenacite from Brazil powdered and plated in a 1:1 mixture with graphite on a graphite carrier, exhibits a quite different TSEE curve (Fig. 10) than the one from an identically prepared sample containing powdered BeO: Si (Thermalox 995). This result indicates that Be_2SiO_4 is at least not the only sensitive compound. Chrysoberyl, another natural beryllium compound, exhibited only erratic TSEE. Clearly, more detailed studies under well controlled conditions are desirable. It can be calculated that the addition of ~6% SiO_2 to the sensitive layer would result in a minimum inherent energy dependence for photons (Fig. 11).

A number of samples was examined which contained varying amounts of other oxides. They had been prepared by hot-pressing at 1600 °C, but were reheated for one hour at 1400 °C prior to evaluation in order to make

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*It should be noted that the peak temperatures have been measured in all cases by a thermocouple at the bottom of the emitting sample (heater/sample interface) and are therefore substantially higher than the actual temperature of the emitting surface. Furthermore, the thermal gradient between bottom and top of the sample depends on thickness and thermal conductivity of the sample. As both may vary, apparent locations of the main peak between approx. 290 and 350 °C have been observed in this study, even if the actual peak temperature is constant and lower (~250 °C).

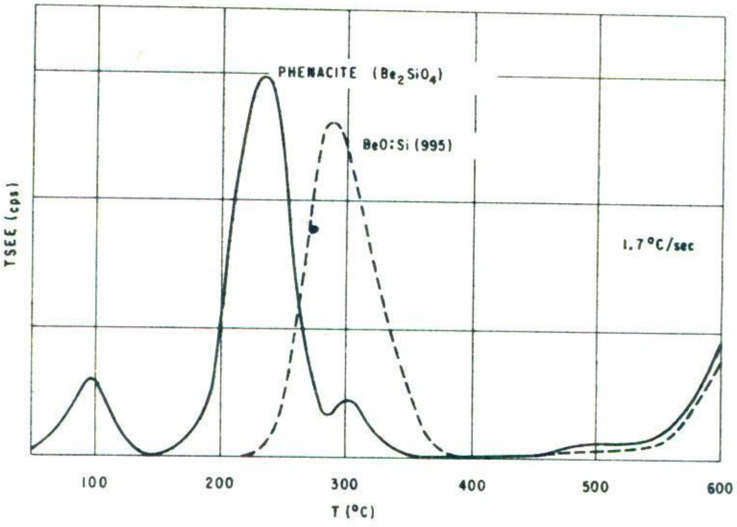

Fig. 10. TSEE of powdered natural Brazilian phenacite (Be_2SiO_4) and of powdered ceramic BeO, mixed with graphite powder and plated on graphite carrier disk.

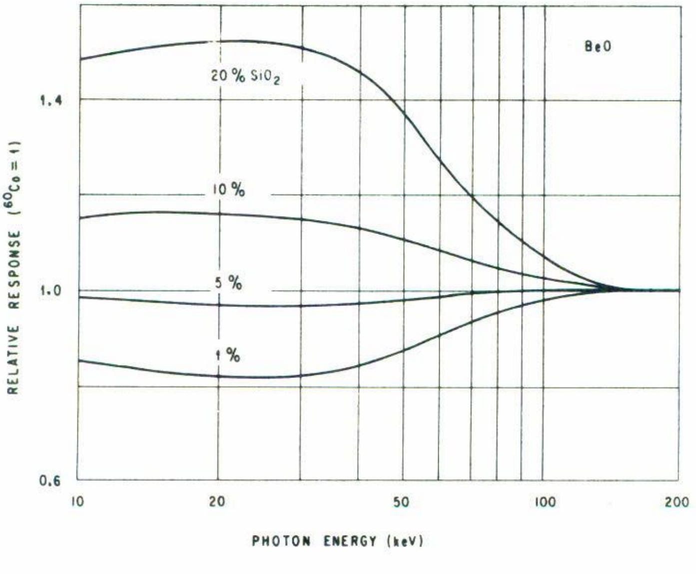

Fig. 11. Calculated energy dependence of the photon response of bulk BeO with varying amounts of SiO_2 homogeneously distributed in it.

them comparable with Thermalox 995. A sample containing a mixture of 1% by weight of 5 $Al_2O_3 \cdot 5\ SiO_2 \cdot 5\ MgO \cdot CaO$ exhibited only one strong peak at ~350 °C, which was very similar to the response of a sample containing 0.5% SiO_2 only.

Samples having 0.5% wt Al_2O_3; 0.5% wt $2MgO \cdot 3\ Al_2O_3$; and 0.5 wt 5 $Al_2O_3 \cdot 5\ SiO_2 \cdot 5\ MgO \cdot CaO$ were found to be quite low in sensitivity. Each of them exhibited two peaks at ~350 and 480 ° C. Heating of those samples to 1600 °C for four hours did not change the peak location, but enhanced the sensitivity (in some similar experiments which were recently reported by Euler et al.,[20] highest sensitivity was found for a mixture of BeO, SiO_2, and ZnO).

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RESUMEN

En este trabajo se estudian las características dosimétricas del BeO utilizando la emisión electrónica térmicamente estimulada (EETE), en particular del BeO: Si con proporciones de activador variables que ha mostrado ser un material con magníficas posibilidades para su uso en la dosimetría de radiación.. Se estudia el comportamiento de otros activadores Li, B y Mn incorporados a la superficie del dosímetro antes del proceso de cocción del material y del MgO, CaO, Al_2O_3 añadidos durante la fabricación del mismo.

Se presentan los resultados obtenidos y se proponen ciertos cambios en la instrumentación electrónica asociada al detector EETE, que han mostrado ser de especial utilidad.