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ABSTRACT

Thermoelectret properties of Beryllium Oxide have been studied in the temperature range RT–600C. Depolarization currents detected during the thermal destruction of the thermoelectret state have been measured under different polarization conditions. The induced polarization has been found to be a uniform volume effect. Two peaks of depolarization current have been detected and their corresponding thermal activation energies measured to be 0.47 eV and 0.65 eV. Electric field enhanced migration of ions with trapping as well as dipolar orientation are proposed to be the contributors to the induced polarization in the formation of the thermoelectret state in BeO.

1 – INTRODUCTION

Considered a potentially good nuclear reactor material due to its physical properties[8], Beryllium Oxide has been studied intensively in recent years. Some sytematic investigations have also been carried out on thermoluminescence (TL) and on thermally stimulated exoelectron emission (TSEE) outputs of samples exposed to ionizing radiation, mainly from the point of view of its application in integrating radiation dosimetry[1]

BeO crystallizes in a wurtzite type structure with the Be^{2+} ions tetrahedrally coordinated with O^{2-} ions and three of these tetrahedral units are joined to form hexagons with the three-fold axis as the polar axis. Brush Thermalox 995 BeO is a commercial form of sintered BeO and has, according to the manufacturer*** an average of 1521 ppm and 1222 ppm of Si and Mg impurities respectively; other impurities are present in lower concentrations. Assuming that Si^{4+} and Mg^{2+} ions enter substitutionally for Be^{2+} in the BeO matrix, the former could, under favorable circumstances, form a defect together with a Be^{2+} vacancy. A charge compensating Be^{2+} vacancy located in a nearest neighbor to the Si^{4+} lattice position forms with the Si^{4+} ion an impurity-vacancy complex which has characteristics of electric dipole and consequently may be oriented under the influence of an external dc field.

It is well known that the cooling of dielectrics in a strong electric field leads in some cases to the appearance of internal polarization within them. The charged dielectric is then said to be in a thermoelectret state, which can be destroyed on subsequent heating. The thermoelectret can be studied on its destruction which is accompanied by the flow of a discharge current in an external circuit. The polarization of the thermoelectret can be due to electric dipole alignment, charge resulting from microscopic displacement of ions with trapping, space charge built up by the migration os ions over macroscopic distances and space charge injected from the electrodes. All these four kinds of charge may coexist in the specimen but only the former two give a uniform volume polarization[6]

Previous work on electrical properties of BeO has been performed covering temperature ranges above 500 C[5]. To our knowledge no work has been published to date on dielectric polarization of BeO.

In this paper results on the formation and destruction of the thermoelectret state in BeO under

different polarization conditions are given to help to identify the mechanism responsible for the observed discharge currents

2 – EXPERIMENTAL

Specimens used in this experiment were commercial sintered BeO ceramic (Brush Thermalox 995).

The thermal depolarization current apparatus consisted of a variable temperature sample chamber, which was operated in vacuum or at controlled gas pressure. The specimen holder electrodes were connected to a Keithley 610 C electrometer. The temperature of the specimen was measured with a Chromel Alumel thermocouple located at the low potential terminal of the specimen holder. Another similar thermocouple was used to drive a temperature programmer which could be set either to keep the sample temperature constant or to raise it at a constant rate; a Keithley high voltage dc power supply was used to polarize the specimen; two recorders were used to measure the depolarization current as a function of temperature, and to monitor the temperature cycles.

The measurement of the thermally stimulated depolarization current was obtained in the following way: a polarizing dc voltage V_p was applied to the specimen at a temperature T_p in the range RT–500 C for a few minutes, the specimen was cooled down to RT with the field still on, the field was turned off and the electrometer connected, and finally the specimen was warmed up to 600 C at a constant rate between 10 and 100 deg/min. The TDC spectrum is the depolarization current as a function of temperature measured during this final heating.

3 – RESULTS AND DISCUSSION

A typical result of the thermal destruction of the thermoelectret state in BeO is shown in Figure 1. This TDC spectrum was obtained during the warming up of a BeO sample previously polarized at 170 C with 600 V and quenched down to room temperature in 15 minutes with the field still applied. The main features of the TDC spectrum of the BeO samples investigated are two current peak maxima located at approximately 100 C (peak 1) and 230 C (peak 2) for a sample heating rate of 40 deg/min. High signal to noise ratio are obtained for measurements under these polarization conditions leading to relatively high charge densities (of the order of 10^{-4} Coul/cm^2).

The two current peaks were resolved by heating the polarized samples to temperatures below 300 C, quenching them to room temperature and reheating up to 600 C to measure the entire TDC spectrum. With this peak clean procedure the thermal activation energies associated with the observed peaks were determined by plotting on semilong paper the depolarization current as a function of the inverse of the absolute temperature. The results are shown in Figure 2.

The activation energies were measured to be 0.47 eV and 0.65 eV for peaks 1 and 2, respectively. These figures will be discussed below after presenting other experimental results.

The change of the amplitude of peak 2 on the previous to polarization annealing temperature is shown in Figure 3. According to this figure in samples preheated at 600 C the induced polarization is higher than in samples heat treated at any other temperature in the range RT–1000 C. The increase in polarization sensitivity for increasing annealing temperatures up to 600 C can be explained if we consider that higher the temperature higher the mobility of the Be^{2+} vacancy, and consequently higher the probability of formation of Si^{4+} – Be^{2+} vacancy complexes or of trapping of Be^{2+} ions which, by their turn, would lead to a higher volume polarization of the specimen. However, the effect of heat treatment at temperatures higher than 600 C is not so easily explainable, but it could be due to chemical reactions such as decomposition or formation of new compounds which could inhibit the impurity vacancy dipole formation and destroy trapping sites.

In Figure 4 the dependence of peaks 1 and 2 current maxima on the polarizing voltages is shown. The total amount of measured charge is directly proportional to the polarizing voltage up to 10^4 V/cm, a value close to the limit of our experimental conditions.

Figure 5 shows TDC spectra for three different polarizing temperatures. In all these experiments the polarizing conditions $t(T_p)$, V_p and $t(V_p)$, and the temperature cycles are kept the same. Samples polarized at different temperatures have similar TDC spectra, the peak temperatures being the same within the experimental error; the difference is in the peak amplitudes: higher the polarizing temperature higher the peak 2 to peak 1 ratio, suggesting that the defects responsible for each current peak have different characteristic relaxation times. The total measured charges namely, the areas under the TDC spectra in Figure 5 are not equal because the polarization time at T_p is not long enough to allow the sample to reach saturation of the induced polarization.

The proportionality shown in Figure 4 as well as the non dependence of peak temperature maxima on the polarizing temperature shown in Figure 5 characterizes the polarization of BeO as a uniform volume polarization[4], limiting our search of the mechanism responsible for the induced polarization to two possibilities: i) build up of trapped charge carriers and ii) ordering of permanent dipoles within the bulk of the sample. We should consider that actually both possibilities might take place during polarization. Perlman[7] suggested that ions trapped in the defects or dislocations in the crystalline regions could give rise to the polarization and the associated depolarization current. Our samples present grain boundaries which may enhance the diffusion energy of Be^{2+} ions[3] making easier the build up of trapped charge. On the other hand the relatively large amount of Si impurities in our samples leads to the second possibility outlined above.

Figure 6 shows schematically the impurity vacancy complex configuration with some of the possible jumps of nearest and next nearest neighbour ions indicated.

Using sets of pairs of values current-temperature afther thermal cleaning procedures to isolate peak 2, and normalized Bucci's equation[4] we have calculated the thermal activation energy (0.65 eV) and the frequency factor ($\sim 7 \times 10^4 sec^{-1}$) by means of a best fitting computer program. The value of the activation energy agreees with the one obtained by the initial rise method but the frequency factor is very low relatively to the normal frequency factor of ionic crystals. The whole calculation procedures are self consistent, i.e. if we assume for example that 0.65 eV is the activation energy for jumping of the Be^{2+} ion in the Y direction (see Figure 6) we calculate the activation energy for jumping in the X direction using a frequency factor twice as that for the Y direction[2] and knowing the temperature at which the peak 1 maximum occurs 0.47 eV is the value obtained in agreement with the value determined by the initial rise method.

Even though the calculation methods agree we should emphasize that the determined value for the frequency factor might be an indication of an overlapping of depolarization current peaks over a continuous distribution of activation energies causing the detection of only one broad peak.

Moreover we think that performing experiments on Thermal Depolarization Currents of BeO single crystals doped with different concentrations of Si might yield informations on the impulity-vacancy reorientation mechanism proposed above.

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Figure 1 — Thermal Depolarization Spectrum of BeO. Conditions of polarization: $T_p = 170°C$; $V_p = 600$ V. The heating rate was 41 deg.min^{-1}.

Figure 2 — Logarithmic plot of current density versus $10^3/T$ for determining by the initial-rise method the thermal activation energies of the discharge current peaks of BeO.

Figure 3 — Effect of previous-to-polarization annealing treatment on the peak 2 current maxima of the thermal depolarization spectrum of BeO. The integrated spectrum is also shown.

Figure 4 — Dependence of peaks 1 and 2 depolarization current maxima of BeO on the polarizing voltage.

Figure 5 — Changes in the TDC spectrum of BeO due to different polarizing temperatures. The arrows point the polarizing temperature for each spectrum.

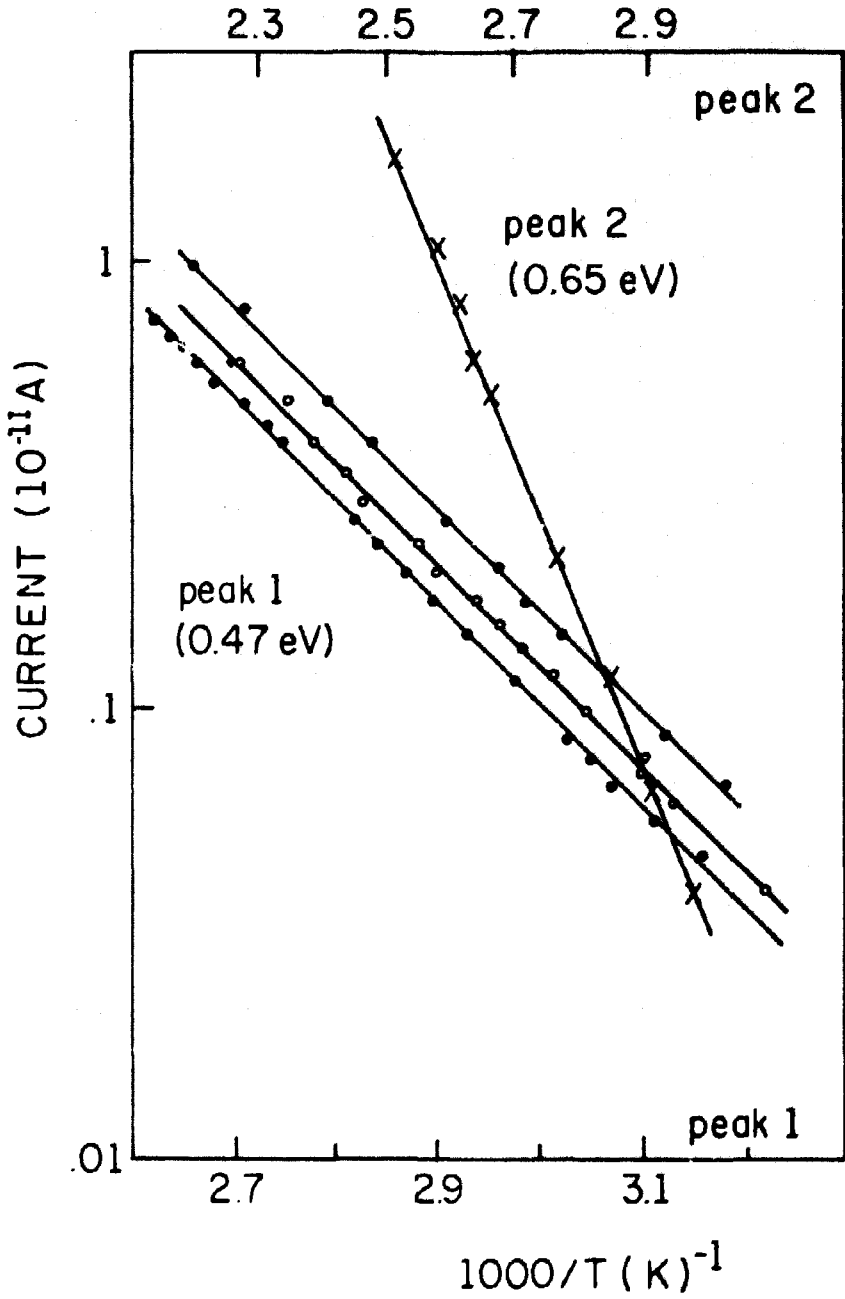Figure 6 — A perspective view of Si-doped BeO crystal (not on scale). See text for more detailed description.
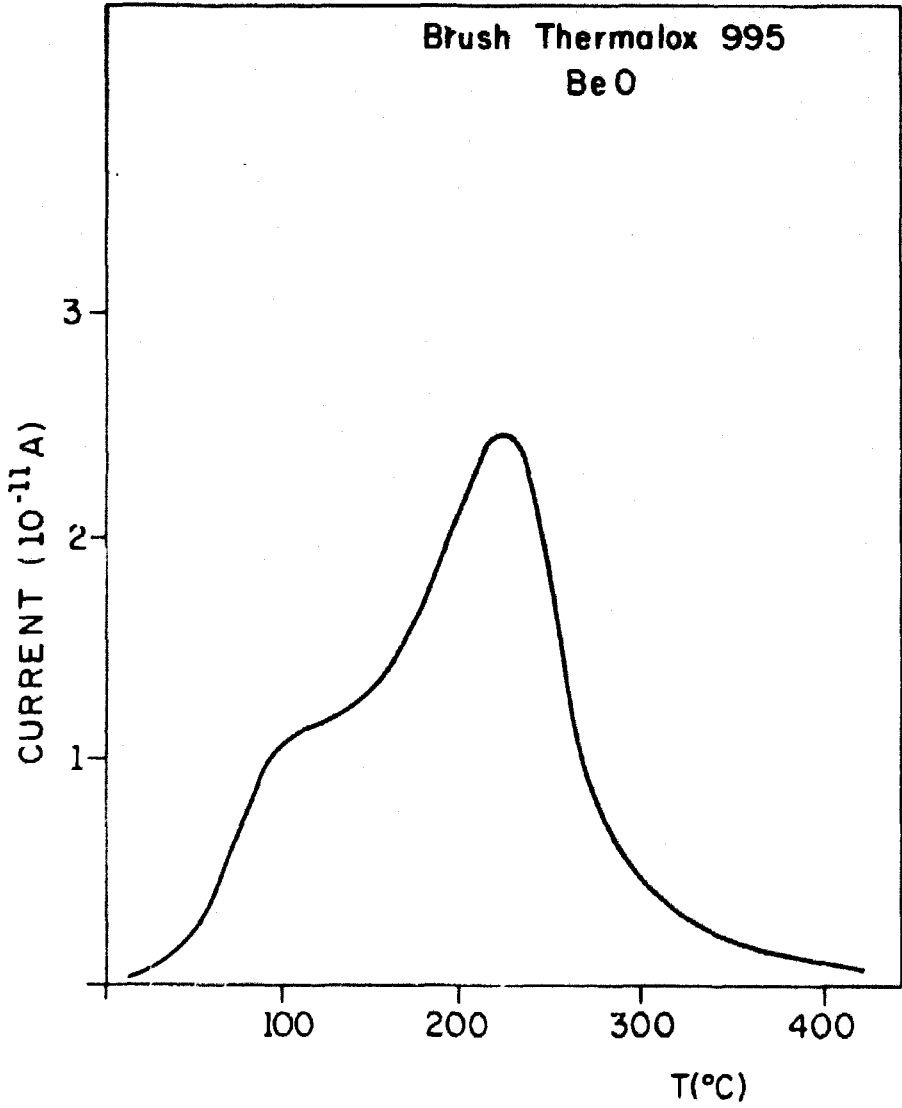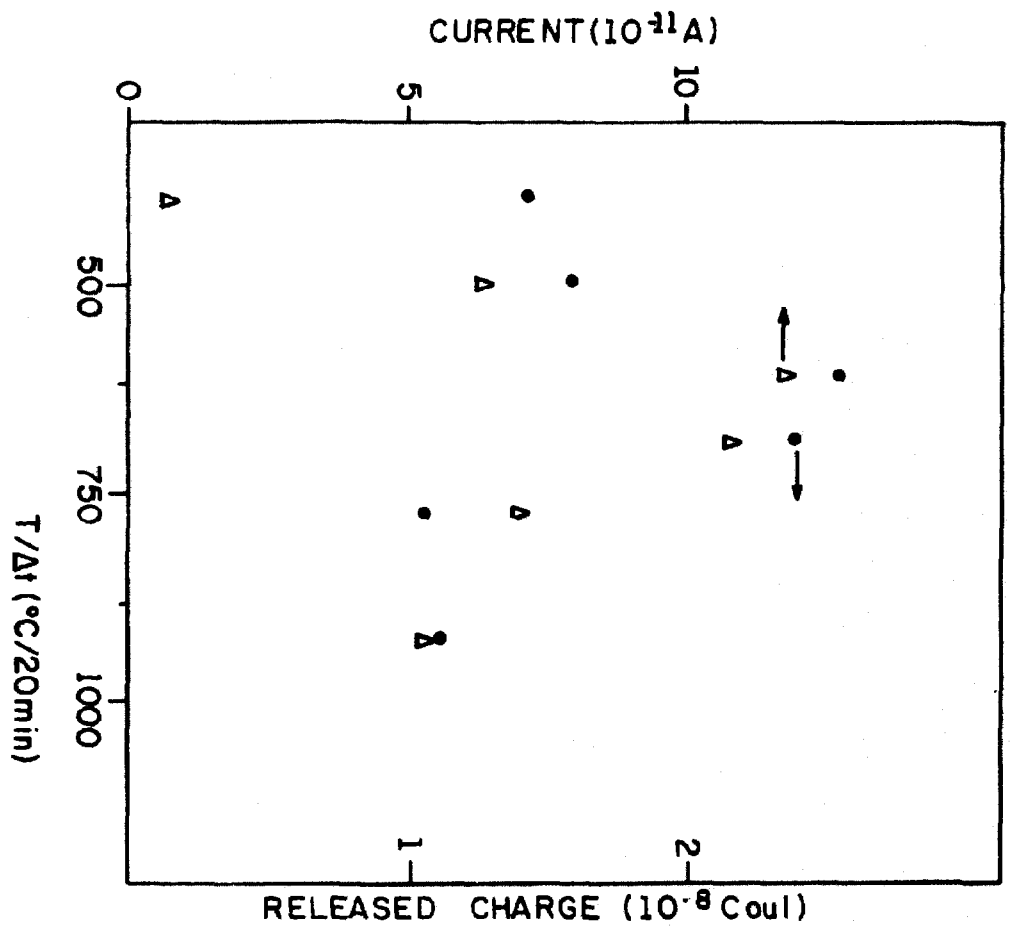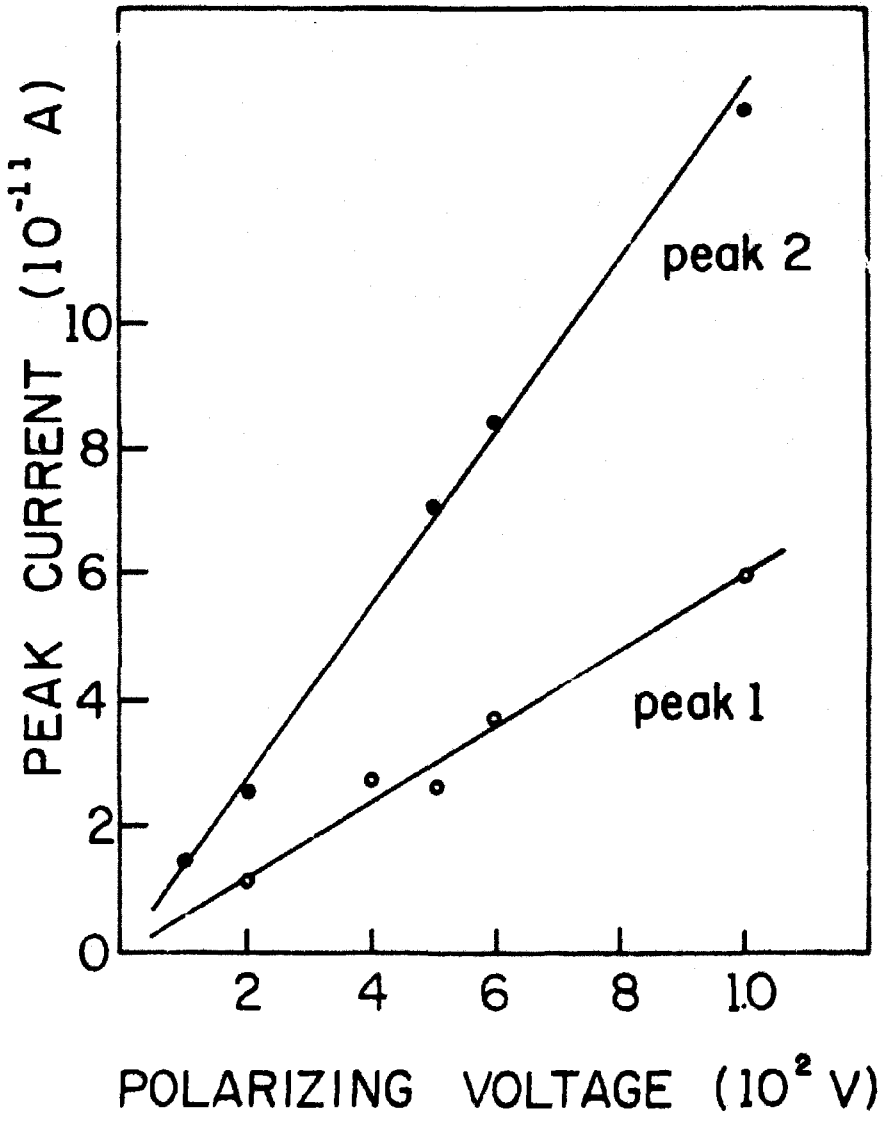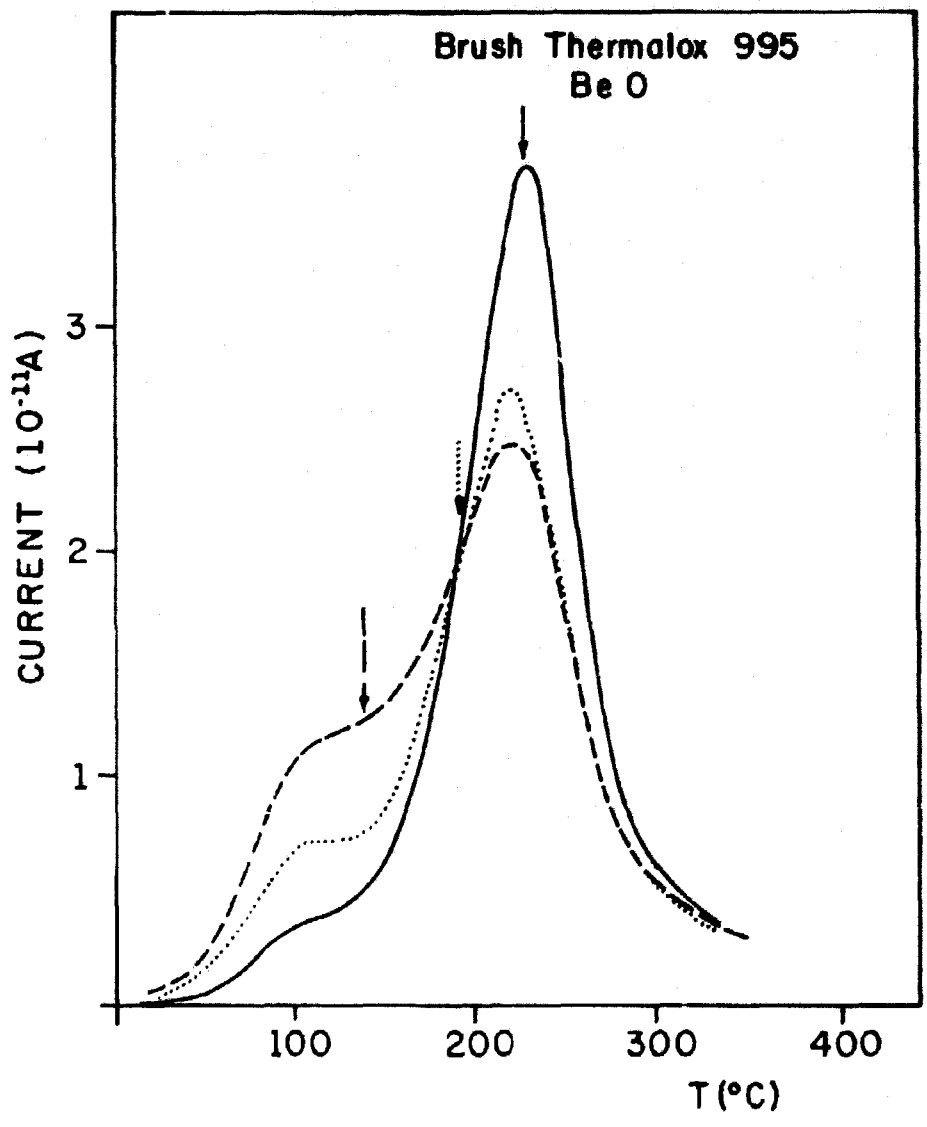
Figure 1

Figure 2

Figure 3

Figure 4

Figure 5
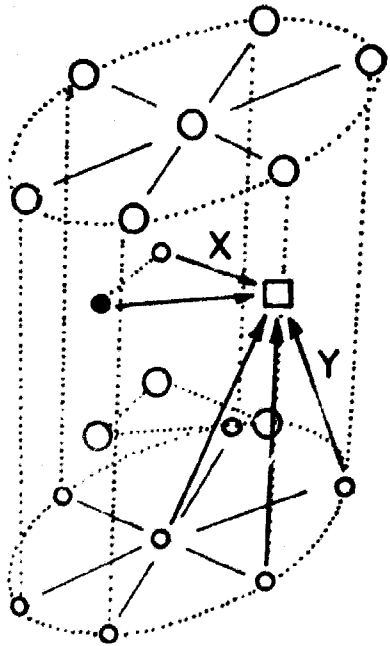
Figure 6

ACKNOWLEDGEMENTS

RESUMO

As propriedades de termoeletreto do oxido de berilio foram estudadas entre a temperatura ambiente e 600°C Correntes de despolarização deretadas durante a destruição termica do estado termoeletreto foram medidas sob diferentes condições de polarização A polarização induzida foi determinada como sendo devida a um efeito volumetrico uniforme Dois picos de corrente de despolarização foram detetados e os correspondentes valores de energias de ativação termica medidos (0 47 eV e 0 65 eV) Dois mecanismos são propostos para explicar a polarização induzida responsavel pelo estado termoeletreto de BeO

a) migração de ions sob ação do campo eletrico dc com consequente armadilhamento em defeitos da rede cristalina e

b) orientação de complexos com caracteristicas de dipolo eletrico presentes nas amostras estudadas

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