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THERMOELECTRET PROPERTIES OF BeO *

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Thermoelectret properties of beryllium oxide have been studied in the temperature range RT–600°C. Depolarisation 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 0.56 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.

Les propriétés de thermoélectret de l'oxyde de béryllium ont été étudiées dans le domaine de températures s'étendant de l'ambiante jusqu'à 600°C. Les courants de dépolarisation détectés durant la destruction thermique de l'état thermoélectret ont été mesurés dans différentes conditions de polarisation. La polarisation induite s'est révélée être un effet de volume uniforme. Deux pics de courant de dépolarisation ont été détectés et leur énergie d'activation thermique correspondantes ont été trouvées égales à 0,47 et 0,65 eV. La migration des-ions favorisée par le champ électrique avec piégeage aussi bien qu'une orientation dipolaire sont proposées comme étant responsables de la polarisation induite dans la formation de l'état de thermoélectret de l'oxyde BeO.

Die Eigenschaften des Elektrets BeO wurden zwischen Rauntemperatur und 600°C untersucht. Die Entpolarisierungsströme, die während des thermischen Abbaus des Elektret-Zustands auftreten, wurden unter verschiedenen Polarisierungsbedingungen gemessen. Die induzierte Polarisation stellt einen einheitlichen Volumeneffekt dar. Es wurden zwei Peaks des Entpolarisierungsstroms bestimmt; die entsprechende gemessene Aktivierungsenergie für die thermischen Prozesse beträgt 0,47 und 0,65 eV. Die durch das elektrische Feld beschleunigte Ionenwanderung einschliesslich der Haftstellenbildung sowie die Orientierung der Dipole tragen vermutlich zur induzierten Polarisation bei der Bildung des Elektret-Zustands des BeO bei.

1. Introduction

Considered a potentially good nuclear reactor material due to its physical properties [1], beryllium oxide has been studied intensively in recent years. Some systematic 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 [2].

BeO crystallizes in a wurtzite type structure with the Be^{2+} ions tetrahedrally coordinated with O^{2-} ions and the 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 circum tances, form a defect together with a Be^{2+} vacancy. A charge compensating Be^{2+} vacancy located in a

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† Brush Beryllium Co., Elmore, Ohio, USA.

nearest neighbor to the Si^{4+} lattice position forms with the Si^{4+} ions 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 upon 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 of ions over macroscopic distances and space charge injected from the electrodes. All four kinds of charge may coexist in the specimen but only the first two give a uniform volume polarization [3].

Previous work on electrical properties of BeO has been performed covering temperature ranges above 500°C [4]. 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 mechanisms 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 610C 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 measurements of the thermally stimulated depolarization current (TDC) 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 fig. 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 min 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

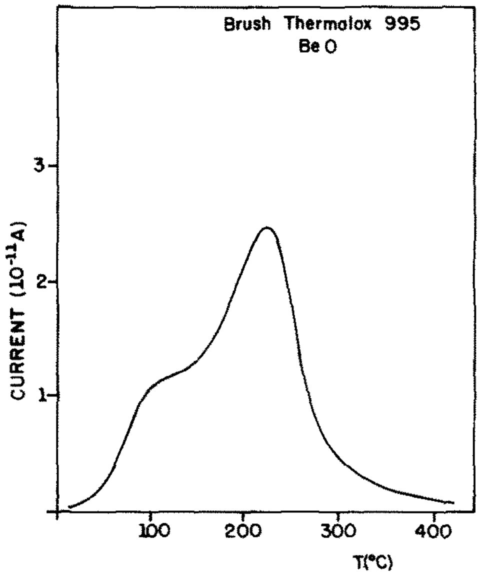

Fig. 1. Thermal depolarization spectrum of BeO. Conditions of polarization: T_p = 170°C; V_p = 600 V. The heating rate was 40 deg/min.

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^{-9} 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 semilog paper the depolarization current as a function of the inverse of the absolute temperature. The results are shown in fig. 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 fig. 3. According to this figure, in samples pre-heated 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 forma-

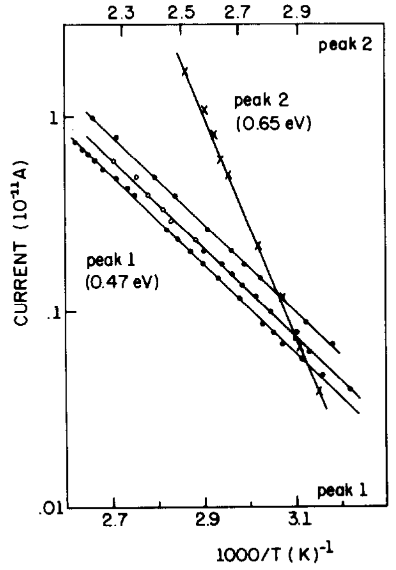

Fig. 2. Logarithmic plot of current versus $10^3/T$ for determining by the initial-rise method the thermal activation energies of the discharge current peaks of BeO.

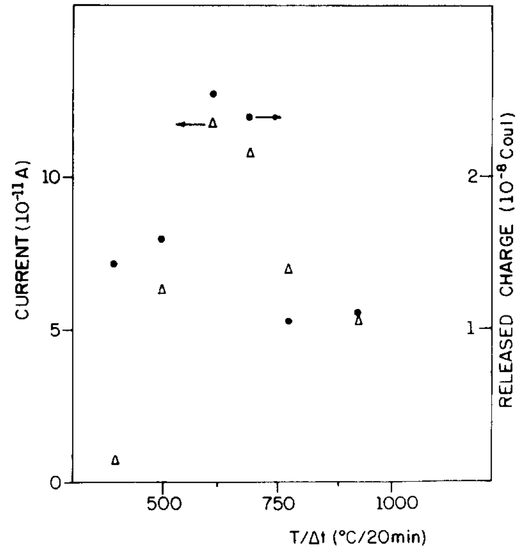

Fig. 3. Effect of previous-to-polarization annealing treatment on the peak 2 current maxima of the thermal depolarization spectrum of BeO. The values for the integrated spectra are also shown.

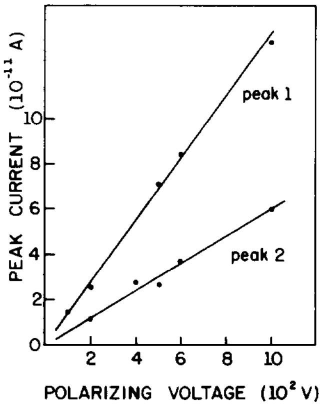

Fig. 4. Dependence of peaks 1 and 2 depolarization current maxima of BeO on the polarizing voltage.

tion of new compounds, which could inhibit the impurity-vacancy dipole formation and destroy trapping sites.

In fig. 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.

Fig. 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; $t(T_p)$ and $t(V_p)$ are the time intervals the sample is maintained at the temperature T_p and under the applied voltage V_p, respectively. 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 fig. 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.

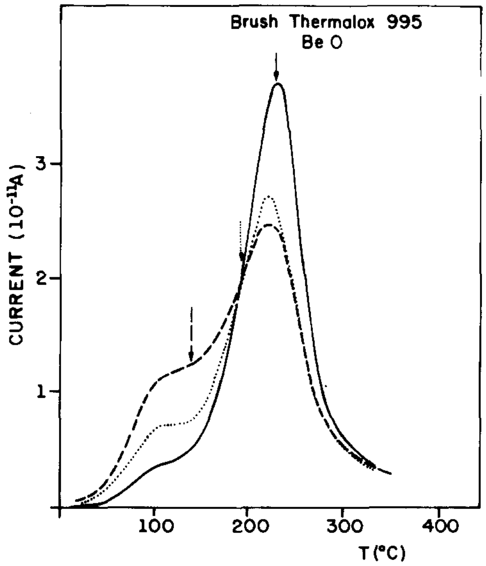

Fig. 5. Changes in the TDC spectrum of BeO due to different polarizing temperatures. The arrows point the polarizing temperature for each spectrum.

The proportionality, shown in fig. 4, as well as the non dependence of peak temperature maxima on the polarizing temperature, shown in fig. 5, characterizes the polarization of BeO as a uniform volume polarization [5], 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 [6] 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 [7] 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.

Fig. 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 of current-temperature after thermal cleaning procedures to isolate peak 2, and normalized Bucci's equation [5] we have calculated the thermal activation energy (0.65 eV) and the frequency factor (~7 X 10^4 sec^{-1}) by means of a best fitting computer program. The value of the activation energy agrees with the one obtained by the initial-rise method, but the frequency factor is very low relative 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

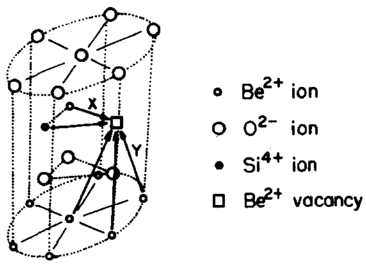

Fig. 6. A perspective view of a Si-doped BeO crystal (not on scale). See text for more detailed description.

the *Y* direction (see fig. 6), we calculate the activation energy for jumping in the *X* direction using a frequency factor twice as that for the *Y* direction [8]. 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 impurities might yield information on the impurity-vacancy reorientation mechanism proposed above.

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