Adsorption-Induced Exoelectron Maximum of BeO Ceramics

By

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Studying the behaviour of the two thermally stimulated exoelectron emission (TSEE) maxima of BeO ceramics at about 270 and 325 °C it can be shown that the TSEE maximum at 270 °C is closely connected with adsorption and desorption processes occurring on the surface of the samples. In particular, this TSEE maximum is strongly influenced by the donor-like behaviour of adsorbed hydrogen on the dehydrated surface of the BeO ceramics. The detailed surface processes leading to the appearance of the TSEE-maximum at 270 °C are discussed.

Durch die Untersuchung des Verhaltens der beiden thermisch stimulierten Maxima der Exoelektronenemission (TSEE) von BeO-Keramiken bei etwa 270 und 325 °C kann gezeigt werden, daß das TSEE-Maximum bei 270 °C eng verknüpft ist mit Adsorptions- und Desorptionsprozessen, die an der Oberfläche der Proben auftreten. Insbesondere wird dieses TSEE-Maximum stark von dem donatorähnlichen Verhalten des adsorbierten Wasserstoffs auf der dehydrierten Oberfläche der BeO-Keramiken beeinflußt. Die Einzelheiten der Oberflächenprozesse, die zum Auftreten des TSEE-Maximums bei 270 °C führen, werden diskutiert.

1. Introduction

Early investigations have shown that sorption can play a decisive role in the exoelectron emission of oxides [1 to 4]. Scharmann and coworkers [5] confirm that for beryllium oxide (BeO), one of the thermally stimulated exoelectron emission (TSEE) maxima is due to the adsorption of oxygen, while Baazov et al. [6], using γ-Al_2O_3 samples, observed an increasing TSEE after adsorption of hydrogen, with a simultaneous appearance of a new emission peak. Kirihata and Akutsu [7], investigating the TSEE of different oxides after adsorption of diverse ions at the surface, pointed out that the peak temperatures are not characterized by the host crystal, but only by the negative ions chemisorbed at the surface.

Studying the so-called surface TSEE maximum of BeO ceramics at about 270 °C, it will be shown that this only occurs when the sample is treated with hydrogen ions in an electric field before exposure to ionizing radiation.

2. Measuring Method

For the measurements of the exoelectrons emitted from ceramic BeO discs (diameter 5.5 mm, thickness 0.5 mm) a windowless methane gas flow counter was used operating in the range of proportionality [8]. The choice of small-size samples was due to the fact that the resolution of two overlapping TSEE maxima is the better, the smaller the temperature gradient in the sample is when heated up. Before each measuring cycle the samples were thermally treated for approximately 1 h at a temperature of 900 °C. All measurements were carried out at a constant heating rate of 1.3 Ks^{-1}. The excitation by means of a γ-ray source (^{60}Co or ^{137}Cs) took place inside the methane gas flow counter to avoid the influence of air humidity. During the read-out by heating up the excited sample, the pulse rate was simultaneously recorded by means of an X–Y recorder.

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3. Results

In general the TSEE adsorption maximum on ceramic BeO at about 270 °C does not occur when the sample has been annealed and exposed to ionizing radiation in air. In this case the "virgin" sample is covered with various kinds of OH groups and Van der Waals' adsorbed water molecules besides a small quantity of organic molecules [9]. During the thermal stimulation by heating the sample to 400 °C, only the main exoelectron maximum at about 325 °C appears (Fig. 1, curve b).

The method adopted for studying the TSEE adsorption maximum on BeO ceramics was very simple. Calling to mind the special treatment of γ-Al_2O_3 samples with hydrogen by Baazov et al. [6], a similar procedure was necessary. Before the admission of hydrogen, the physisorbed water molecules have of course to be desorbed from the surface under investigation. For that reason, the BeO sample was heated to 400 °C inside the counter in the dried methane atmosphere. In this process, a readsorption of desorbing water molecules must be avoided. After cooling to 20 °C, a positive high voltage of 3.5 kV was switched on the counting wire and the sample was irradiated by a γ-ray source (^{60}Co or ^{137}Cs). The γ-rays penetrating the metal walls of the counter create Compton electrons and photoelectrons, some of these reaching the methane atmosphere inside the counter. Because a sufficiently high voltage at the counting wire is switched on, the usual electron multiplication process in the proportional counter takes place. In the electron avalanche region, the counter gas is dissociated and among other heavier positive ions, the lightest ones H^+ and H_2^+ are produced. According to the studies of the radiolysis of methane by the absorption of energy from 100 eV electrons, the H^+ and H_2^+ ions constitute 0.71% of the total positive ions [10], this proportion also being constant for electrons of much higher energy [11]. As they drift toward the outer wall, these slowly moving positive ions can, among other things, reach the BeO sample and become partially adsorbed. After the high voltage was switched off, the sample was excited by γ-rays inside the counter. During linear thermal stimulation of the excited sample, a new emission maximum appears at a temperature of about 270 °C (Fig. 1, curve a). It is to be noted that this new emission maximum totally vanishes when the sample is in contact with humid air before excitation by γ-rays or after a second exposure and stimulation run without the treatment by hydrogen ions mentioned above.

Assuming that adsorption centres cause this TSEE maximum, it may be supposed that ion treatment is responsible for the generation of these centres. Hence the number of ions produced will influence the TSEE yield of this maximum, provided that the excitation is constant. Unfortunately, the number of positive ions generated in the methane atmosphere cannot be directly measured with the proportional counter used. But if a constant gas multiplication factor is assumed in the counter during operation, the ratio of positive ions to electrons is also constant. Thus, the electrons recorded during ion treatment will be a measure of the number of positive ions generated. Fig. 2 shows the increasing exoelectron yield N_{EE} from adsorption centres with an increasing number of recorded electrons (pulses), whilst Fig. 3 shows the
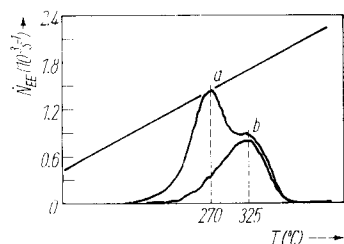

Fig. 1. Exoelectron emission $\dot{N}_{EE}$ of ceramic BeO (a) after and (b) before admission of hydrogen. T heating temperature

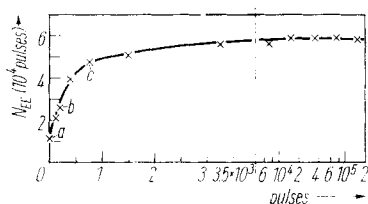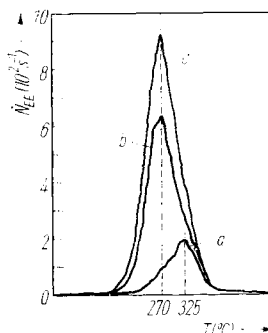Fig. 2   Fig. 3

Fig. 2. TSEE yield N_{EE} of ceramic BeO as a function of recorded electron avalanches (pulses)

Fig. 3. The change of the two TSEE maxima of sintered BeO at about 270 and 325 °C for three points of Fig. 2. T heating temperature

developing of the maximum for the points a, b, and c in Fig. 2. The rapid saturation effect of the generated adsorption centres is noteworthy. While the relative number of positive ions varies by a factor of about 10^3, the exoelectron yield increases by a factor of only about 6, provided that the fluence of the exciting γ-rays is constant. This behaviour of the TSEE adsorption maximum implies that the generation of this peak is strongly governed by a surface mechanism, since the low-energy ions can affect only the adsorbed surface layer of the sample.

In order to elucidate the adsorption nature on the TSEE closely connected with the number of occupiable surface sites, the exoelectron yield and the change of emission maxima were studied in dependence on increasing high voltage during ion treatment, and the fluence of exciting γ-rays was also changed. Repeating the above-mentioned procedure prior treatment of the sample inside the counter, but beginning the ion treatment at lower voltages, the new emission maximum at about 270 °C does not appear as long as no gas multiplication effect takes place, which means that positive hydrogen ions are not generated in sufficient amount. After excitation by γ-rays, the TSEE maximum is observed at only about 325 °C, which is scarcely influenced by the adsorption process (Fig. 4, curve a). Only if the starting voltage for the gas multiplication in the methane atmosphere inside the counter is reached and positive hydrogen ions are produced, being partially adsorbed at the sample surface, the TSEE adsorption maximum appears at about 270 °C (Fig. 4, curves b to d). With increasing high voltage during ion treatment, both the total number of exoelectrons and the emission maximum at 270 °C show a sharp simultaneous increase (Fig. 5, points c and d). This steep increase of the total TSEE beginning at about
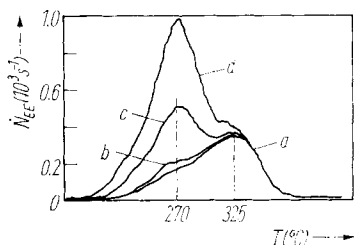
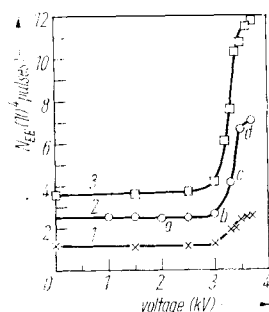Fig. 4. The change of the two TSEE maxima of ceramic BeO for four points of Fig. 5. T heating temperature

Fig. 5. TSEE yield N_{EE} of sintered BaO as a function of increasing high voltage at the counting wire during hydrogen ion treatment. Exposure in air to radiation from a γ-ray source: (1) 5, (2) 10, (3) 15 mR

3 kV is due to the fact that with increasing high voltage, the electrical field strength between the anode and the dielectric BeO grows. As a consequence, the gas amplification in the counter becomes larger, and more and more electrons and positive ions are created in each avalanche near the counting wire. Checking the pulse height distribution, one observes that the number of large electron avalanches increases while the number of small electron avalanches decreases, the total number of the avalanches, however, remaining constant.

The observed change in the total exoelectron yield is the result of increasing photon fluence after ion treatment, which is doubled from curve 1 to curves 2 and 3 in Fig. 5. Taking into account the above-mentioned fact, more and more active TSEE centres produced by ion treatment are occupied during increasing excitation by γ-rays. As shown in Fig. 2, a certain saturation is also indicated in Fig. 5, independent of the photon fluence used. Unfortunately, higher voltages cannot be reached as this would set off gas discharges inside the counter.

As mentioned above, the TSEE maximum at about 270 °C totally vanished with the admission of humid air. This effect, of course, only takes place when the surface of the sample is covered with hydrogen ions, but has not yet been excited by γ-rays. Only after excitation the new TSEE peak is stable against water vapour in the air.

Using commercially available methane gas, a small amount of water vapour with a partial pressure of about 0.13 Pa has to be taken into account. In further investigations, the BeO was exposed to undried methane gas inside the counter after prior ion treatment. Only after storage times of between 4 and 100 min a constant excitation by a γ-ray source took place. The results of these measurements are shown in Fig. 6. The total TSEE yield decreases with increasing exposition time, in which the adsorption-induced TSEE peak is mainly affected by "humid" methane gas. This is demonstrated for three exposition times (Fig. 6, points a, b, c) in Fig. 7, showing the diminution of the emission maximum at 270 °C. Only if the sample is exposed to humid air for one minute, the new TSEE almost totally vanishes (Fig. 6, point d, and Fig. 7, curve d). The fact that a steady state in the TSEE yield is already reached after one hour, is noteworthy indicating that further low pressure humidity in the methane gas does not affect the adsorption-induced maximum. In comparison a drastic change takes place after a short storage period in humid air.
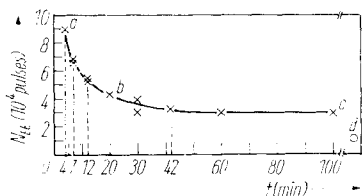

Fig. 6. The diminution of the TSEE yield N_{EE} of ceramic BeO as a function of the storage time t in wet methane
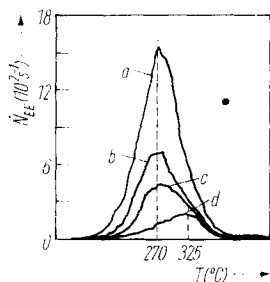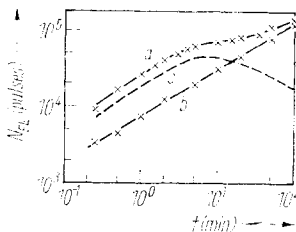
Fig. 7   Fig. 8

Fig. 7. The change of the two TSEE maxima of ceramic BeO for four points of Fig. 6. T heating temperature

Fig. 8. TSEE yield N_{EE} of sintered BeO as a function of increasing time of exposure to a γ-ray source. (a) Samples covered with hydrogen ions adsorbed up to saturation; (b) samples without hydrogen ions; (c) curve obtained by subtracting the TSEE yield of curve b from that of curve a

During the preceding set of measurements, the exposures applied by the γ-ray sources were relatively low, not exceeding a few hundred mrd's. In the following, an increasing exposure by secondary Compton electrons and photoelectrons was studied to elucidate the behaviour of the adsorbed hydrogen ions by intense electron bombardment. After prior treatment, the samples were covered with hydrogen ions adsorbed up to saturation and then exposed to a γ-ray source. Taking the exposition geometry constant, the time was varied between 2.5 and 100 min. As Fig. 8 (curve a) demonstrates, the total TSEE yield of both emission maxima increased up to a certain exposition time of about 5 min in which the exposure by electron bombardment was relatively low. After reaching a critical electron fluence, a change in the proportionality between the TSEE yield and the exposure could be observed, showing a slower increase of exoelectrons recorded with increasing exposure.

Simultaneous measurements of the exoelectron emission in dependence on the exposure applied to BeO samples which had not undergone the above-mentioned special prior treatment, however, show a straight line up to an exposure time of 100 min (Fig. 8, curve b). Obviously, during an intense electron bombardment, the exoelectron emission maximum at 270 °C only was affected. Taking into account that adsorption centres cause this emission maximum, an electron-induced desorption of these centres takes place causing the decrease of the emission maximum at 270 °C. This effect was demonstrated by Euler et al. [5] investigating the changes of the so-called O-peak on BeO powder samples during an intense electron bombardment. Following from the conclusions in the above-mentioned paper, adsorbed particles which act as exoelectron centres leave the surface by electron-induced desorption and are lost to the exoelectron emission. This is demonstrated by curve c in Fig. 8
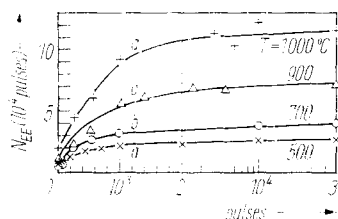

Fig. 9. TSEE yield N_{EE} as a function of recorded electron avalanches (pulses) of BeO ceramics annealed at 500, 700, 900, and 1000 °C before each measuring cycle
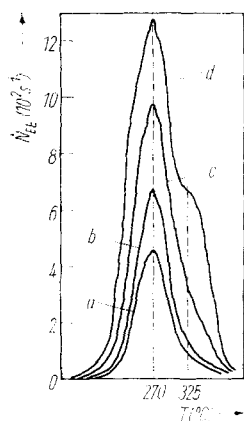
Fig. 10. The change of the two TSEE maxima of sintered BeO for four points of Fig. 9. T heating temperature

which was obtained by subtracting the TSEE yield of the BeO sample, showing only the emission maximum at 325 °C (curve b) from the total TSEE yield (curve a). On the other hand, it is known [12] that radiation can produce desorption by rupture of a chemical bond holding an adsorbate or surface group to a solid. In this case ionization and excitation produced by radiation are important factors, and heavy particles are not required for the removal of the fragment, the thermal energy being sufficient when a suitable bond has been broken. Thus electrons and X-rays can be effective.

Studies of the catalytic exchange reaction (H_2 to D_2) for ZnO have shown that a change in the ratio between cations and anions in the ZnO lattice in favour of the cations is observed by sintering at higher temperatures [13]. This means that more Zn ions of lower valency, which are effective sites for hydrogen chemisorption, are produced at the surface. A similar effect should be expected for BeO which also has a wurtzite-type crystal lattice.

With the results in mind, demonstrated in Fig. 2, "virgin" BeO samples were selected and heated up to temperatures in the range between 500 and 1000 °C before each measuring run. After heating up the samples inside the counter in order to desorb physisorbed water molecules, an increasing ion bombardment was applied. Afterwards, all samples were irradiated by a constant γ-ray fluence. As Fig. 9 shows, the total TSEE yield increases with the increasing annealing temperature of the sample before the measurements. In accordance with conclusions referring to the change of the catalytic ability of ZnO in dependence on the sintering temperature, one is compelled to assume that the same effect takes place for BeO, too. That is to say, by heating the BeO ceramics in steps at higher temperatures before the ion bombardment, more and more Be ions of lower valency are produced at the surface, available for the chemisorption of hydrogen. In consequence of this increasing chemisorption, more acitive surface sites available for exoelectron emission are created. This is demonstrated in Fig. 10 for four annealing temperatures (points a, b, c, and d in Fig. 9), showing a marked growth of the adsorption-induced exoelectron maximum at 270 °C.

4. Discussion

Taking the whole of the above-mentioned results into account as regards the surface nature of the TSEE maximum at 270 °C, some remarks are necessary concerning the mechanism of this phenomenon. First, the surface constitution of the "virgin" sample must be ascertained. By measurements of the infrared absorption spectra of thin self-supporting pressed BeO pellets, isolated OH groups are known to occur on the BeO surface apart from the OH groups, bound by H bridges, and Van der Waals' adsorbed water molecules [9, 14]. Following from the conclusions in [9], in the temperature range up to 300 °C physisorbed water molecules become desorbed, whilst in the higher temperature range hydroxyl groups bound by H bridges recombine and then desorb.

On heating the samples to 400 °C during special prior treatment, more and more thermally stronger bound OH groups bound by H bridges are bared on the surface of the sample under investigation and can be reached by hydrogen ions during subsequent ion bombardment. From measurements of the electrical conductivity on ZnO and other crystals it is known that the adsorption of hydrogen molecules or atoms leads to a decrease of the work functions for the majority carriers and to an increase of the electrical conductivity [6, 15 to 20]. The authors in [12] conclude that adsorption of hydrogen occurs on oxygen lattice ion sites with the formation of (OH)$^-$ ions and the liberation of electrons to the conduction band.

The latter effect is most important because the number of free carriers in an insulator is very small before hydrogen adsorption. The energy imparted during subsequent irradiation with Compton electrons and photoelectrons may be used either to induce chemical reactions in the solid itself or to influence certain adsorption processes occurring at the surface of the solid. In the present case, the energy imparted by electrons results in the transformation of thermally stronger bound OH groups bound by H bridges into thermally weaker bound groups. As has been shown in [22], due to this thermal transformation of the OH groups a renewed desorption of physisorbed water molecules and recombined OH groups can be observed by heating the dehydrated BeO sample to 400 °C. Following the conclusions in [6], new emission centres for TSEE are created due to hydrogen adsorption, these centres being either closely connected with the adsorption sites or identical to them.

Contrary to the ability of the adsorbed hydrogen to act as an electron donor, water adsorbed at the surface of an oxide solid forms a particularly efficient recombination centre for electrons and holes [18]. With regard to this effect, the disappearance of the TSEE maximum at 270 °C can be explained when the hydrogen-covered BeO sample has been in contact with humid air before excitation by γ-rays. This explanation does not hold for the stability of the adsorption-induced TSEE maximum when the sample is exposed to humid air after γ-ray excitation. Further investigations are therefore needed to explain the contrary behaviour of the TSEE maximum at 270 °C.

As has been noted above, the surface of oxide solids becomes the more non-stoichiometric in favour of the cations, the higher the treatment temperature before use is. On the other hand, an increase of the TSEE total yield after annealing the BeO samples at higher temperatures is observed. With regard to the adsorption-induced TSEE maximum at 270 °C, the non-stoichiometric excess Be ions at the surface behave as additional adsorption sites. Thus it is reasonable to assume that hydrogen is chemisorbed as a proton on O$^-$ and as a negative ion on Be$^+$. After dissociation of this complex, the proton moving to the next oxygen ion forms another hydroxyl ion. On heating the sample after excitation by a constant γ-ray fluence, the above-mentioned increase of the TSEE yield is observed due to the thermal recombination and desorption of the adsorbed radicals.

5. Conclusion

The above-mentioned investigations clearly show that the TSEE maximum at 270 °C for BeO ceramics is closely connected with adsorption and desorption processes occurring on the surface of the samples. The appearance and disappearance of this maximum is strongly controlled by the donor-like behaviour of adsorbed hydrogen giving rise to the release of electrons to the conduction band. After the excitation by ionizing radiation and subsequent heating up the sample, these excess electrons become partially detected as exoelectrons during the recombination and desorption of the surface radicals.

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