THE USE OF THERMALLY STIMULATED DEPOLARIZATION CURRENTS TO STUDY GRAIN GROWTH IN CERAMIC THORIUM DIOXIDE

R. Muccillo and L. L. Campos

PUBLICAÇÃO IEA 526 IEA - Pub - 526	MAIO/1979

CONSELHO DELIBERATIVO

MEMBROS

Klaus Reinach — Presidente
Roberto D'Utra Vaz
Helcio Modesto da Costa
Ivano Humbert Marchesi
Admar Cervellini

PARTICIPANTES

Regina Elisabete Azevedo Beretta
Flávio Gori

SUPERINTENDENTE

Rômulo Ribeiro Pieroni

PUBLICAÇÃO IEA 526
IEA - Pub - 526

MAIO/1979

THE USE OF THERMALLY STIMULATED DEPOLARIZATION CURRENTS TO STUDY GRAIN GROWTH IN CERAMIC THORIUM DIOXIDE

R. Muccillo and L. L. Campos

CENTRO DE PROTEÇÃO RADIOLÓGICA E DOSIMETRIA
CPRD - AMD 040

INSTITUTO DE ENERGIA ATÔMICA
SÃO PAULO - BRASIL

Série PUBLICAÇÃO IEA

INIS Categories and Descriptors

B23

Thorium dioxide
Grain growth
Depolarization

Nota: A redação, ortografia e conceitos são de responsabilidade dos autores.

THE USE OF THERMALLY STIMULATED DEPOLARIZATION CURRENTS TO STUDY GRAIN GROWTH IN CERAMIC THORIUM DIOXIDE(*)

R. Muccillo and L. L. Campos

ABSTRACT

Depolarization Current Spectra resulting from the destruction of the thermoelectret state in polycrystalline ThO_2 samples have been detected in the temperature range 100 K–350 K. The induced polarization is found to be due to migration of charge carriers over microscopic distances in the bulk of the specimens with trapping at grain boundaries. Moreover the density of charge carriers released from trapping sites, upon heating the cooled previously dc biased specimen, decreases for increasing sintering temperature, suggesting the use of the technique to the study of grain growth in the bulk of ceramic oxides.

Early in 1964 the Thermally Stimulated Depolarization Current (TSDC) technique was proposed to the study of divalent impurity-vacancy complexes in alkali halide crystals[1]. The method has since then been applied to aliovalent impurity-doped ionic crystals, to the determination of relaxation parameters (thermal activation energies and jump frequencies for reorientation of complexes[2], to study the kinetics of solubility, precipitation and dissolution[2], and to study color center phenomena[2,5,7]. It has also been used recently to study the thermoelectret state of BeO[6]. We propose here another application of the technique: the determination of average grain size and the study of grain growth by using charge carriers as probes being diffused in the bulk of ceramic oxides. Its main advantage is the possibility of studying grain growth in the bulk of the specimens. Other available techniques deal with surface measurements.

The TSDC experiments were done using Thorium Dioxide of two origins: commercial Ceralloy 908C(**) and 1000 psi/3 min cold pressed discs with nuclear grade ThO_2 powder as starting material. All the specimens had diameter of 13 mm and thickness of 1 mm. The TSDC apparatus consisted of a sample chamber in which the temperature of the specimen could be controlled in the range 100 K–350 K under vacuum, connected to a high voltage power supply and to a Keithley 610C electrometer. The lowest detectable current was in the 10^{-14} A range. The experimental sequence to obtain the TSDC spectrum was as follows: (i) polarize the specimen with V_p (10^2 V – 10^3 V) at a temperature T_p (150 K–350 K) during t_p (10 s – 600 s); (ii) cool the specimen down to 100 K; (iii) turn the electric voltage off; (iv) connect the electrometer and heat the specimen up to 350 K with a constant rate; (v) repeat the above sequence with $V_p = 0$ V. Steps (iv) and (v) give the TSDC spectrum and the background current spectrum, respectively. In Figure 1 is shown a typical TSDC spectrum of ceramic ThO_2 obtained under the following experimental conditions:

$T_p = 300$ K, $V_p = 500$ V, $t_p = 120$ s, and a heating rate of 4 deg/min. At least five current maxima are resolved at approximately 190 K, 225 K, 260 K, 285 K and 305 K. These peak temperatures were determined by carrying out systematic peak-cleaning experiments consisting of partial depolarizations of

(*) Research partially sponsored by Comissão Nacional de Energia Nuclear.

(**) Ceradyne, Inc., Santa Ana, Cal. U.S.A.

Approved for publication in IEA series in December 1978.

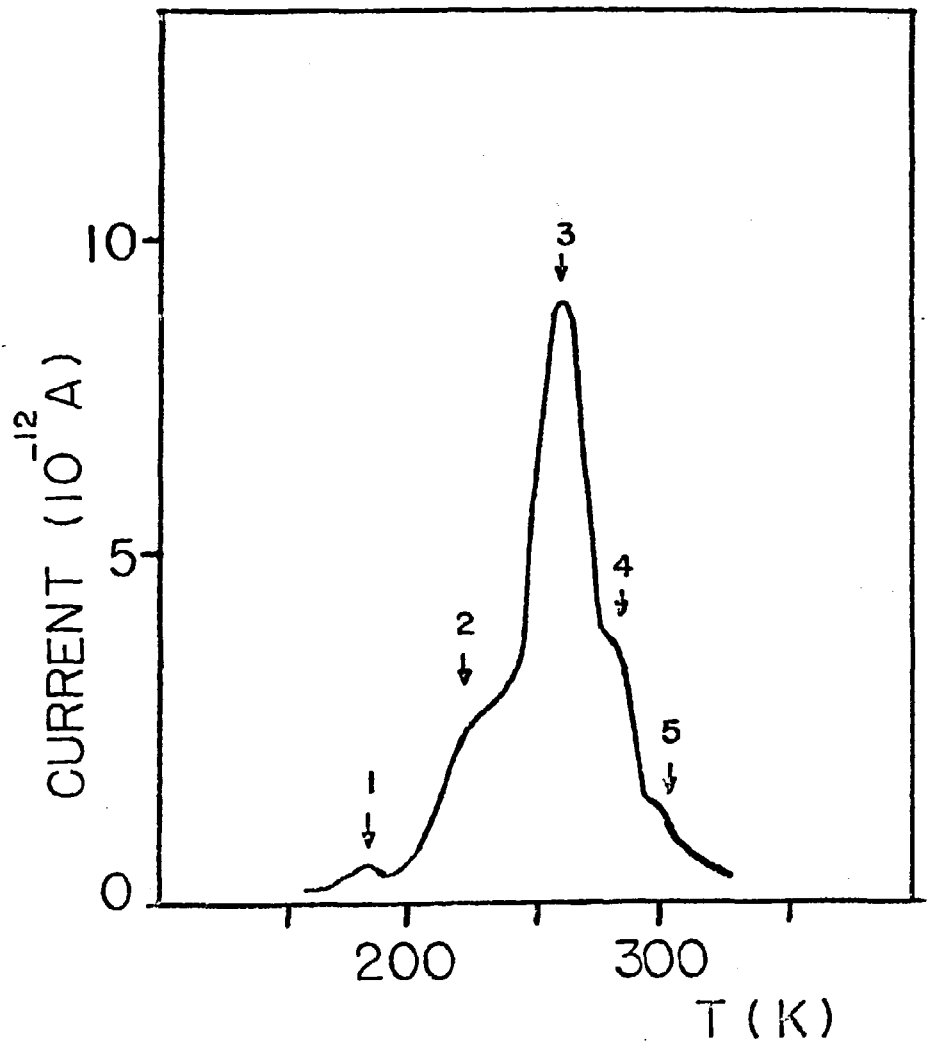

Figure 1 – Thermally Stimulated Depolarization Current spectrum of polycrystalline Thorium Dioxide; polarization conditions: T_p = RT, t_p = 120 s, E_p = 5000 V/cm; heating rate: 4 deg/min

the specimen to temperatures between 200 K and 300 K, cooling down the specimen to 100 K, and then measuring the entire TSDC spectrum. A thorough work is presently being carried out to find out which are the defects responsible for the structure shown in the TSDC spectrum of ThO_2 in that temperature range; determination of relaxation parameters as well as preferential effects and non-stoichiometry effects might help the understanding of the mechanisms responsible for the observed relaxations. The specimen at 100 K after the electric field is turned off shows a persistent charge; in other words, the specimen is in a thermoelectret state. The heating up of the specimen to obtain the TSDC spectrum corresponds to the destruction of the thermoelectret state, and the normalized charge associated with this process, namely, the ratio of the area under the spectrum to the heating rate, is also related to the induced polarization and is taken as a measure of the thermoelectret ability of the specimen. Its value for polycrystalline ThO_2 was measured as 10^{-11} C/cm^2.V.

The dependence of the amplitude of the depolarization current on the applied polarizing voltage is shown in Figure 2. A linear dependence up to 6000 V/cm is found leading to a characterization of the induced polarization as a volume polarization. The decrease in the induced polarization for dc fields higher than 6000 V/cm is found to be due to current leakage through the specimen via grain boundaries reducing the actual value of the internal dc field.

The thermoelectret state of ThO_2 is tentatively ascribed to the formation of space charge in the bulk of the specimen in the sense that each crystallite becomes polarized and that grain boundaries are acting as internal blocking electrodes. This charge distribution is frozen in at low temperatures even after the electric field is removed. The charge-associated to the detected polarization is a heterocharge due migration of charge carriers over microscopic distances with trapping according to the theory of Gross[3]. Furthermore we could also speculate that grain boundaries are paths for diffusion of charge carriers when a dc field is applied to the polycrystalline specimen. The question now is how could the microstructure of a ceramic sample influence its electric polarization. If this polarization is related to migration of charge carriers, this migration could either proceed withing the crystallite until it is blocked at grain boundaries, or it could be accelerated in the grain boundaries themselves which are known to be diffusion paths, or both. In the first assumption, the higher the average grain size, the lower the density of trapping sites for the electric field-activated migration of charge carriers. This would lead, in its turn, to a lower induced polarization of the specimen. This reasoning proved to be correct after analysing the results of TSDC speriments in samples sintered at different temperatures, which is the usual procedure to obtain grain size variation. The results are shown in Figure 3 where the induced polarization (plotted here as the peak 3 amplitude) is plotted as a function of sintering temperature. All the TSDC experiments were obtained in the same manner, i.e., the polarization conditions and the temperature cycles were kept the same. These results show that higher the sintering temperature lower the depolarization current amplitude and consequently, the induced polarization is lower the higher the average grain size. There is a disagreement in this behavior for samples heat treated at 900 C. This is not easy to explain but some experiments are under way to verify whether it is related to pore shrinkage which is known to occur at this temperature[4].

A simple model for the dependence of the induced polarization on the average grain size was developed taking into account that charge carriers jump under the action of a electric field and are blocked at grain boundaries; the total frozen in polarization of the specimen is assumed to be proportional to the density of trapping sites, which is inversely proportional to the average grain volume. This means that the induced polarization determined during the destruction of the thermoelectret state depends on the average grain size according to the equation $P + P_o = \text{constant}/L^3$ where P stands for the induced polarization, L for the average grain size and P_o is a constant. In Figure 4 the induced polarization (represented here by the peak 3 current amplitude) is plotted as a function of L^{-3}. The L values were determined by X-Ray line broadening techniques. The results shown in Figure 4 are in agreement with the above equation proving that the measured polarization can be used to determine relative average grain size and to the study of grain growth in polycrystalline samples. TSDC experiments with ThO_2 single crystals are under way in order to know the contribution of impurity-compensating vacancies to the relaxation, and to compare with the observed relaxations in polycrystalline samples.

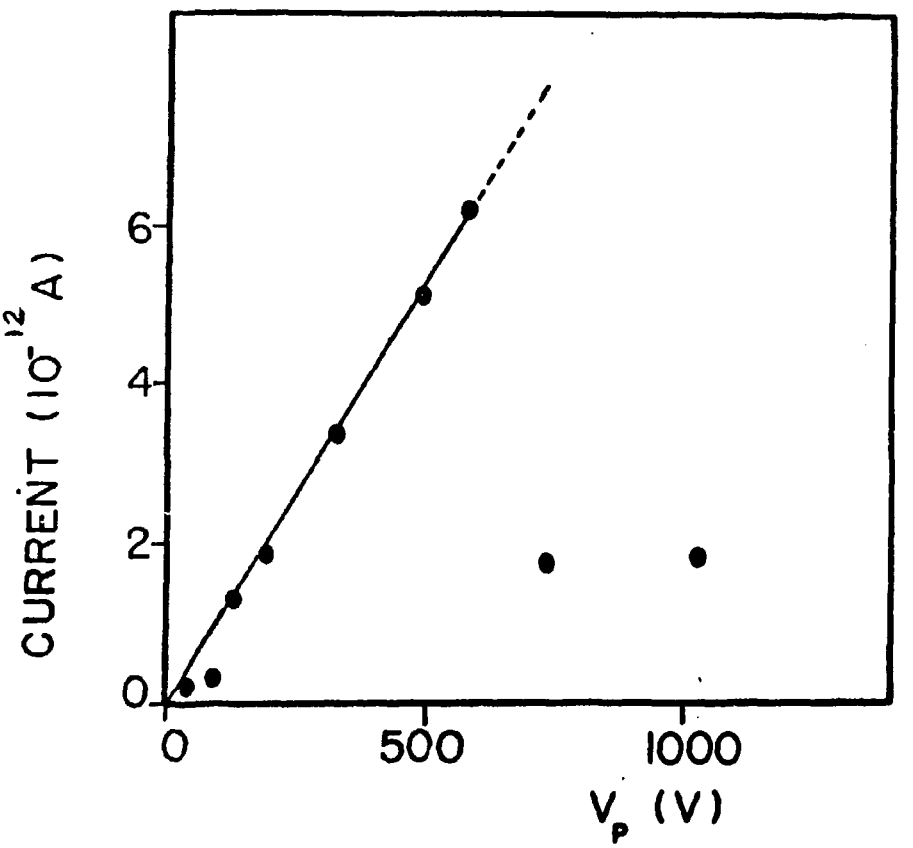

Figure 2 – Dependence of peak 3 maximum amplitude on the polarizing voltage for ThO_2 polycrystalline samples

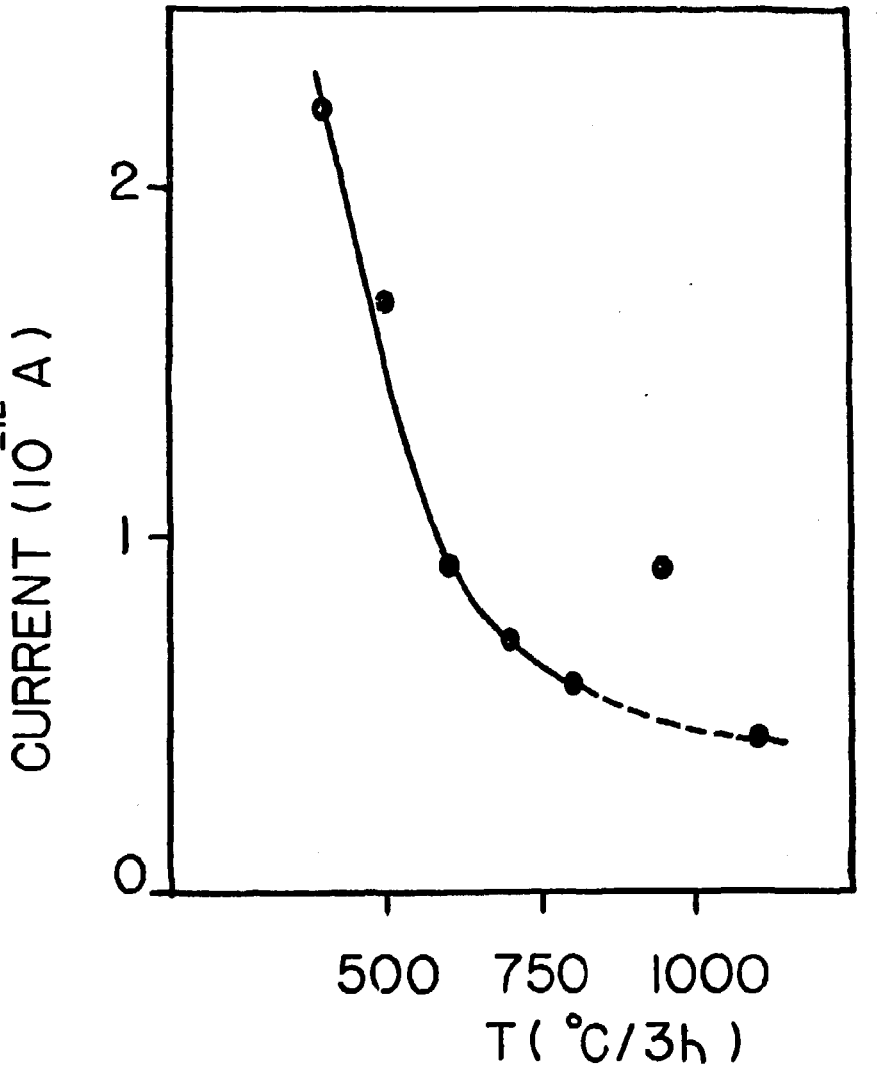

Figure 3 – Dependence of peak 3 maximum amplitude of TSDC spectrum of polycrystalline ThO_2 on the sintering temperature; sintering atmosphere: air

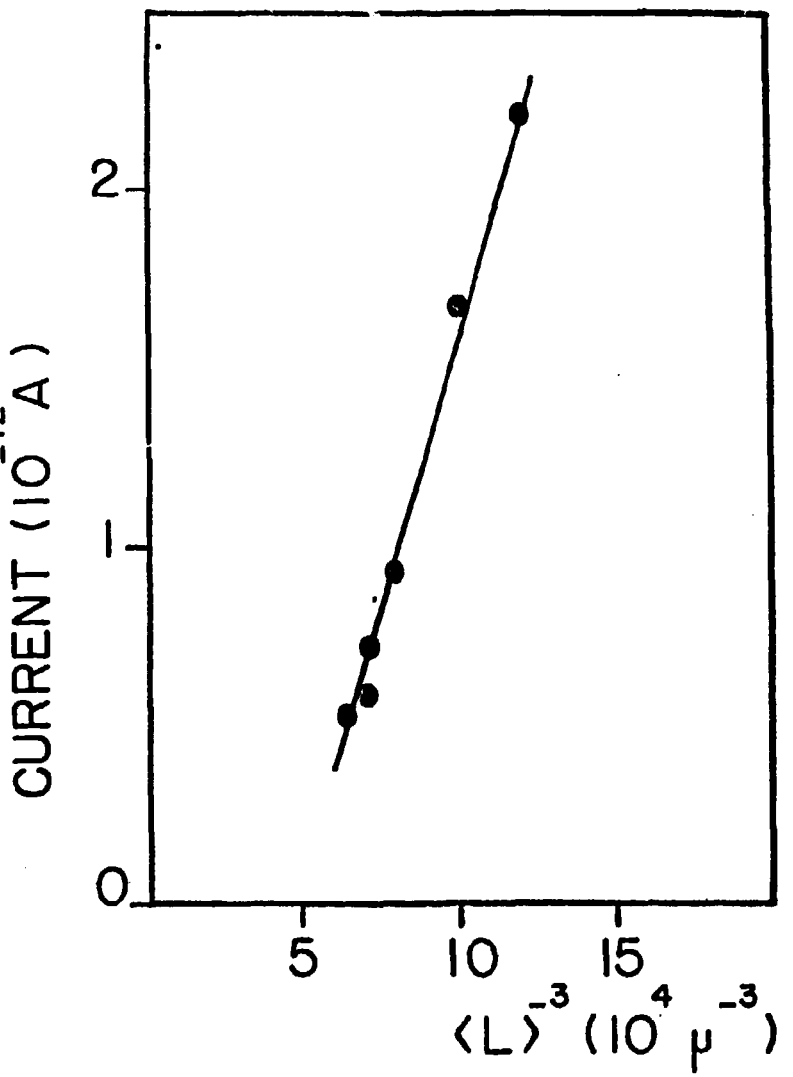

Figure 4 – Correlation between the induced polarization (plotted here as the amplitude of peak 3 in the TSDC spectrum) and the average crystallite size of polycrystalline ThO_2

Even though this will not change propositions of the present work, it will help the understanding of the basic mechanisms involved in the observed depolarization spectrum of ceramic ThO_2.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. K. Imakuma for helping in the X-Ray analysis.

RESUMO

Espectros de Correntes de Despolarização resultantes da destruição do estado termo-eletreto em amostras policristalinas de ThO_2 foram detectados entre 100 K e 350 K. Foi verificado que a polarização induzida é devida à migração de portadores de carga através de distâncias microscópicas no volume das amostras. Além disso, foi encontrada uma correlação entre a concentração de portadores de carga – carga associada à destruição do estado termoeletreto – e a temperatura de sinterização, evidenciando a possibilidade de uso da técnica de medidas de Correntes de Despolarização para o estudo de crescimento de grãos em amostras cerâmicas.

REFERÊNCIAS BIBLIOGRÁFICAS*

1. BUCCI, C. & FIESCHI, R. Ionic thermoconductivity. Method for the investigation of polarization in insulators. *Phys. Rev. Lett.*, 12(1):16-9, Jan. 1964.

2. CAPELLETTI, R. & FIESCHI, R. *Int. symp. on electrets and dielectrics.* [s.l.], Academia Brasileira de Ciências, 1977. p.131.

3. GROSS, B. *J. chem. Phys.*, 17:866, 1949.

4. KINGERY, W. D., ed. *Kinetics of high-temperature processes: conference on the... held at MIT Endicott House, Dedham, Mass., June 23-27, 1958.* Cambridge, Mass., MIT, 1959. (Technology press book in science and engineering).

5. MARAT-MENDES, J. N. & COMINS, J. D. *Cryst. Lattice Defects*, 6:141, 1975.

6. MUCCILLO, R. & BLACK, A. R. Thermoelectret properties of BeO. *J. nucl. Mater.*, 61:66-70, 1976.

7. MUCCILLO, R. & ROLFE, J. Effect of irradiation on impurity-vacancy dipoles in KBr crystals doped with strontium. *Phys. Status Solidi, B, Basic Research*, 61:579-87, 1974.

(*) As referências bibliográficas relativas a documentos localizados pelo IEA foram revistas e enquadradas na NB-66 da ABNT.

INSTITUTO DE ENERGIA ATÔMICA
Caixa Postal, 11049 – Pinheiros
CEP 05508
01000 – São Paulo – SP

Telefone: 211-6011
Endereço Telegráfico – IEATOMICA
Telex – 011-23592 IENA BR