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THERMAL BEHAVIOUR OF PEROVSKITE CERAMICS AS A MATRIX FOR ENCAPSULATION OF HAZARDOUS ELEMENTS

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Emanation thermal analysis (ETA) was used to characterize thermal behaviour of the perovskite ceramics designed as a matrix for the encapsulation of high level radioactive waste. The perovskite ceramics (composition $CaTiO_3$ where small admixtures of Nd and Ce simulated the radioactive elements Cm and Pu, respectively) was prepared from sol-gel precursors by hot pressing at 1250°C/29 MPa for 2 h. The chemical durability of the ceramics was tested by leaching in the solution with pH 2 at 90°C/2 months. ETA results of "as-leached" and "as-prepared" perovskite ceramics samples were compared and evaluated by means of a mathematical model. Three temperature ranges of the annealing of structure defects in the "as-prepared" sample were determined from the decrease of radon release rate in the ranges 280-560, 800-960 and 960-1200°C, respectively. One annealing step was determined for the 'as-leached' sample from the decrease of radon release rate in the range of 800-950°C.

Keywords: annealing, diffusion, emanation thermal analysis, perovskite $CaTiO_3$, radioactive waste encapsulation, radon, sol—gel method, structure irregularities

Introduction

The main advantage of the perovskite based ceramics as the matrix for the encapsulation of hazardous elements consists in high chemical durability and high absorption ability for heavy elements e.g. transuranium elements that compose high level radioactive waste (HLW). The safe final disposal of these elements, that are produced as waste from nuclear facilities, has to fulfill many requirements. One of the requirements is to ensure high chemical durability as well as radiation and thermal stability of the ceramics forms where the radioactive nuclides were encapsulated or immobilized [1, 2].

In this study the emanation thermal analysis (ETA) [3-6] was used to characterize the thermal behaviour of the perovskite ceramics samples, prepared from sol-gel based precursors and tested for chemical durability by leaching according to internationally recommended protocol. The protocol recommended by the materials characterization center (MCC) [7] was used in testing the chemical durability. A mathematical model [8] was used to evaluate the ETA results of the "as-leached" and "as-polished" samples.

In our previous studies the ETA was already applied in the characterization of microstructure development of advanced ceramics as well as finely dispersed or porous inorganic materials and their precursors. A good agreement was found between the results of ETA, XRD, SEM and surface area determined from nitrogen adsorption-desorption using BET method [9-11].

Experimental

Preparation of perovskite based ceramics samples

The perovskite based ceramics was prepared from the sol-gel precursors using tetra-isopropyl titanate ($Ti(C_3H_7O)_4$) and aluminium *sec*-butoxide (A1(C4H9O)3). Calcium hydroxide as well as small amounts of neodymium and cerium, that simulated transuranium elements, were added into the slurry after hydrolysis of alcoxides [12]. A pre-determined excess of methanol was added to a mixture of tetra-iso-propyl titanate ($Ti(C_3H_7O)_4$) and aluminium *sec*-butoxide ($A1(C_4H_9O)_3$). Water in excess required for complete hydrolysis of the methoxide mixture was slowly added and coagulates were formed. Room temperature slurring for ~8 h eliminated flocculent aggregates and resulted in a suspension resembling a

white paint. The evaporation of alcohol by heating on a hot plate (~120°C) for ~6 h reduced the volume by about 2/3. The addition of calcium hydroxide and of neodymium and cerium, simulating the transuranium elements in proportions appropriate to its formulation, was followed by mixing at room temperature for more than 1 h and by heating the slurry on a hot plate (140-150°C) for ~5 h to reduce its volume until it had the consistency of thick cream. This approach yielded a precursor which was chemically homogenous at sub-micron levels; the dried precursor possessed the surface area 250 m^2 g^{-1}.

The sample of bulk perovskite ceramics was pre pared by hot pressing in argon containing 5% hydrogen at the temperature of 1250°C/29 MPa for 2 h. In the ceramics with the nominal chemical composition $Ca_{0.98214}(Nd_{0.00790}Ce_{0.00996})Al_{0.01786}Ti_{0.98214}O_3$, the Nd and Ce rare earth elements were assumed to be triva-lent and to be incorporated in the Ca site via an Al^{3+} substitution on a Ti^{4+} site [12].

The surface of the sample was polished prior to the investigation by ETA, XRD or SEM. The two investigated samples of the perovskite ceramics were denoted “as-polished” and “as-leached”, respectively. The “as-leached” sample was prepared by leaching of the “as-polished' sample in the solution with pH 2 at the temperature of 90°C/2 months [7, 12]. Both “as-polished” and “as-leached” samples were labeled for the ETA measurements.

Testing methods

Leaching test of chemical durability

The international testing protocol recommended by MCC [7] was used in testing chemical durability of the perovskite ceramics sample.

The sample was subjected to a pH 2 buffer solution (0.05M KC1+0.013M HC1) at 90°C for 2 months over four 7-day leach periods and a 28-day leach period [12].

The dissolution of perovskite was supposed to proceed according to the following scheme:

$$CaTiO_3+2H^+ \rightarrow Ca^{2+}+TiO_2(\text{anatase})+H_2O$$

Emanation thermal analysis

In ETA [3-6] the radon released from samples was used to monitor changes in solid surfaces and microstructure of subsurface layers under in situ conditions of heating and cooling. The ETA measurements were carried out by using a modified Netzsch-DTA equipment, Model 404, under following experimental conditions: heating in argon+6% hydrogen (flow rate 50 mL min"1) at the rate 5 K min ' and subsequent cooling from 1200°C to room temperature at the same rate.

The ETA results are expressed as the ratios of the rate of radon release to the rate of radon formation in the solid, determined as E (in relative units) $E=A_\alpha/A_{total}$, where A_α is the α-radioactivity of radon released in unit time from the labeled sample, and A_{total} is the total y-radioactivity of the sample. The A_{total} value is proportional to the rate of radon formation in the sample. Semiconductor and NaI(Tl) detectors are used for the a- and y-radioactivity measurements, respectively.

Labeling of samples for ETA measurements

The “as-polished” and “as-leached” perovskite ceramics samples were labeled by the deposition of drops of acetone solution that contained ^{228}Th and ^{224}Ra as parent nuclides of ^{220}Rn. Atoms of ^{220}Rn were formed from ^{228}Th and ^{224}Ra atoms by spontaneous a-decay and introduced into the subsurface of the sample owing to recoil energy (85 keV $atom^{-1}$). The specific activity of the samples was 10^5 $Bq*g^{-1}$. The maximal penetration depth of radon atoms in perovskite was 118 nm, as calculated by Monte Carlo method using TRIM code [13]. SEM equipment (Hitachi, Type X-650) with an energy dispersive X-ray analyzer (Kevex) and X-ray diffraction device (Rigaku, type Geiger-flex) were used for morphological observation and phase identification, respectively.

Results and discussion

Thermal behaviour of perovskite ceramics samples

Figure 1 depicts ETA results of perovskite ceramics samples measured during heating up to 1200°C and subsequent cooling in argon+6% hydrogen; curves 1 and 1’ correspond to the “as-polished” sample, curves 2 and 2' correspond to the “as-leached” sample, respectively. We assumed that the intense in-crease of the radon release rate E(T) observed on heating of the “as-polished” sample from 20 to 100°C (curve 1, Fig. 1) was due to the radon diffusion from cracks caused by surface polishing. The SEM

micrograph in Fig. 2 confirmed that the surface of the 'as-polished' sample contained micro-cracks. The annealing of the polishing defects and other subsurface structure irregularities in this sample was characterized by ETA as the decrease of radon release rate E(T) in the range of 280-560°C (Fig. 1, curve 1). The two steps decrease of the E(T) observed in the range of 800-1200°C was supposedly due to the annealing of grain boundaries and/or remaining latent pores. It was determined by XRD (Fig. 3) that the altered surface of the 'as-leached' sample contained anatase. The thickness of the altered anatase containing layer was estimated by using the amount of Ca in the leach-ate to be approx. 40 μm [12].

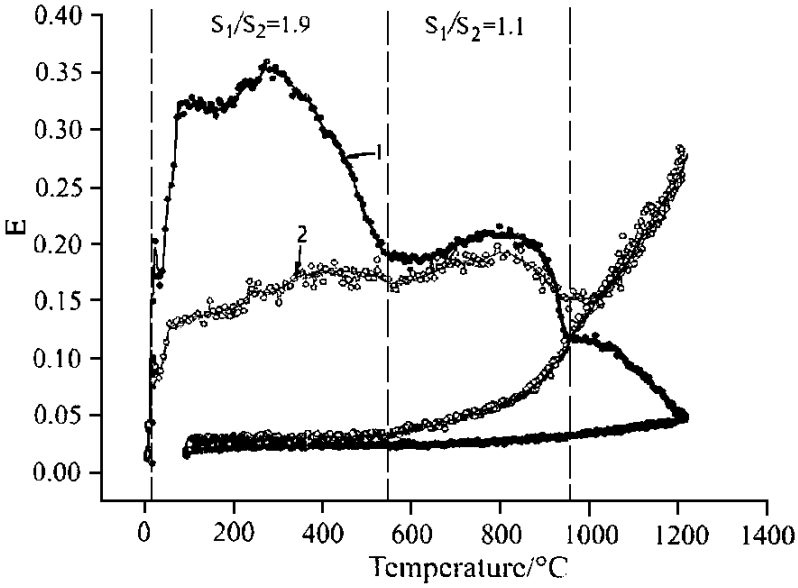

Fig. 1. ETA results of bulk perovskite ceramics measured during heating to 1200°C and subsequent cooling in argon+6% hydrogen. Curves 1 and 1' - correspond "as-polished" sample, curves 2 and 2' – "as-leached" sample, respectively

By comparing the temperature dependences of the radon release rate E(T) measured on heating from 30 to 560°C for the "as-leached" and "as-polished" samples (Fig. 1, curves 2 and 1, respectively) it was assumed that the polishing defects and possibly other subsurface microstructure defects in the "as-polished" sample were eliminated in course of the leaching.

The only decrease of the radon release rate observed on the ETA curve of the "as-leached" sample in the temperature range of 800-950°C (curve 2, Fig. 1) was ascribed to the microstructure changes in the titania containing altered surface of the sample. It is of interest that in the same temperature range of 800-960°C a decrease of the radon release rate E(T) was observed both with the "as-leached" sample and with "as-polished" sample, however, with a lower intensity in former one.

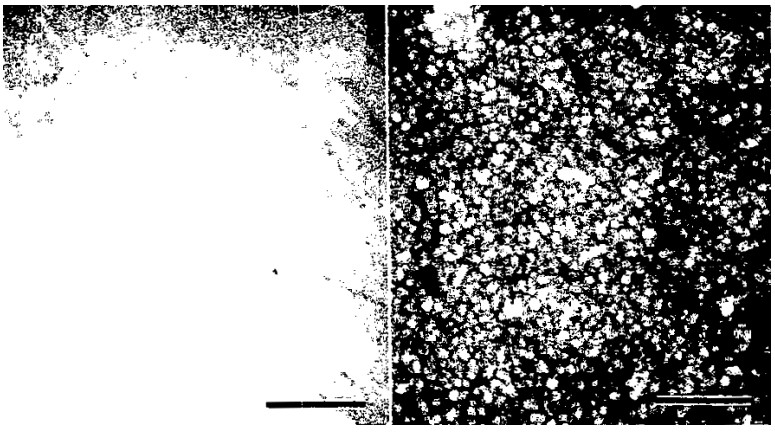

Fig. 2 SEM micrographs of 1 – "as-polished" and 2 – "as-leached"

Assuming that the radon diffusion release from the samples was controlled by the structure irregularities, the ETA results were used to assess the number of the structure irregularities in the respective samples and their annealing on subsequent heating in the selected temperature ranges. Therefore, we compared ETA results of "as-polished' and "as-leached' samples (curves 1 and 2, Fig. 1) in the ranges 20-560 and 560-960°C, respectively to assess the number of structure irregularities that served as radon diffusion paths. The ratio of the number of diffusion paths as obtained by the integrating the ETA curves in the temperature range 20-560°C is S=1.9 and in the range 560-960°C it is S=1.1.

The increase of E observed on heating of the 'as-leached' sample beyond 1000°C (curve 1, Fig. 1) was ascribed to the radon diffusion by volume mechanism. Such enhanced radon release was not observed with the 'as-polished' sample. On the contrary, the decrease of the radon release took place in this range due to the annealing of the radon diffusion paths in the sample Subsurface.

From the comparison of the ETA results measured during cooling of the both samples of the perovskite ceramics (curves 1' and 2', Fig. 1) it followed that the radon mobility in the samples considerably differed. We assumed that the higher amount of the structure irregularities in the 'as-

polished' sample enhanced the sample densification on heating that is expressed by a lower radon mobility in this sample heated to 1200°C. The activation energy of radon diffusion calculated from the ETA cooling curves of the "as-polished" and "as-leached" samples in the temperature range 800-1200°C as determined by using Eq. (4) (next paragraph) are 62±5 and 136±3 kJmol^{-1}, respectively.

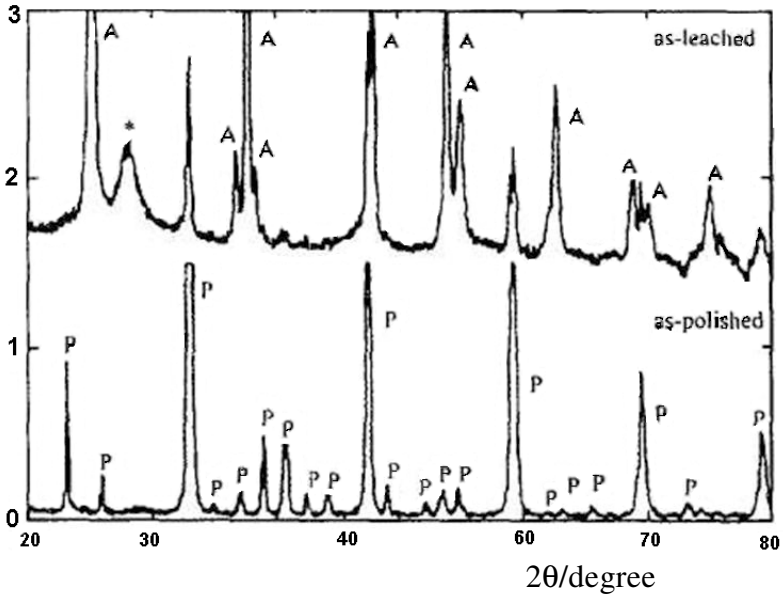

Fig. 3 XRD patterns of "as-polished" and "as-leached" perovskite ceramics samples; A - anatase, P - perovskite and * - unidentified lines, respectively

Modeling and evaluation of ETA results

A mathematical model [8] was used for the evaluation of the ETA experimental data of radon release from the perovskite samples investigated in this study. In the evaluation it was supposed that the radon solubility in solids is negligible and lattice defects, such as vacancy clusters, grain boundaries and pores, served as traps for radon atoms. At the same time, the structure defects of the ceramics served as radon diffusion paths. A survey of various factors influencing the migration of inert gases in solids is given in [4]. In the ETA the used radionuclides of ^{228}Th and ^{224}Ra are a quasi-permanent source of radon that is formed by the spontaneous a-decay and incorporated into the perovskite samples by recoil energy (85 keV atom^{-1}) to the maximal depth of 118 run [13]. It was supposed that the radon release was controlled by the diffusion along surface and subsurface structure irregularities, interface boundaries as well the volume diffusion (the latter process takes place at elevated temperature, e.g. for the perovskite samples on heating above 800°C). The temperature dependence of the radon release rate, E(T) can be written in a simplified way as

$$E(T) = E_D(T) * \Psi(T) \qquad (1)$$

The term E_D is characterizing radon permeability along structure irregularities and the function Ψ(T) is characterizing the decrease of the number of the radon diffusion paths.

In the mathematical model used for the evaluation of ETA results it was supposed that the temperature dependence of the radon release rate, E_D(T), due to diffusion involves parameters which determine the radon diffusion, taking into account the average diffusion length of radon $L_D = \sqrt{\frac{D}{\lambda}}$, where D is the radon diffusion coefficient and λ is the radon decay constant.

Following expression was used in the modeling of the temperature dependence of the radon release rate due to diffusion, E_D,

$$E_D(T) = \frac{3}{r_0}\sqrt{\frac{D(T)}{\lambda}}\left\{\coth\left[r_0\sqrt{\frac{\lambda}{D(T)}}\right] - \frac{1}{r_0}\sqrt{\frac{D(T)}{\lambda}}\right\} \qquad (2)$$

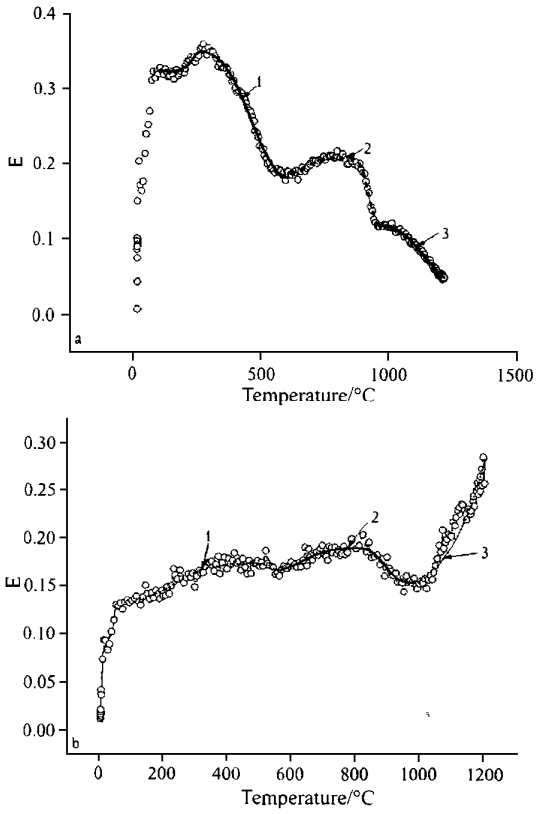

Fig. 4 Comparison of ETA experimental results (points) and model curves 1, 2 and 3 (lines) describing thermal behaviour of perovskite ceramics; a – "as-polished" sample, b – "as-leached" sample

the radon diffusion coefficient D(T) was supposed

$$D(T) = D_0 \exp\left(-\frac{Q_D}{RT}\right) \qquad (3)$$

where D_0 is pre-exponential factor depending on number of diffusion paths and their availability for radon atoms migration, Q_D is activation energy of radon migration both the activation energy of the escape of radon atoms from the traps in the solid sample and of the migration along diffusion paths in the solid, R is molar gas constant, T is temperature in K.

It was assumed that the radon release from labeled samples took place by several diffusion mechanisms, i.e. by the diffusion along surface and subsurface structure irregularities.

The descending character of the Ψ(T) function was simulated by using following expression

$$\Psi(T) = 0.5\left(1 + erf\frac{1-\frac{T_m}{T}}{\frac{\Delta T\sqrt{2}}{T}}\right) \qquad (4)$$

where *erf* is the sign for the integral Gauss function, T_m is the temperature of maximal rate of the annealing of the defects which serve as radon diffusion paths, ΔT is the temperature interval of the respective solid-state process. Equation (4) was used in this study for the description of the annealing of radon diffusion paths during the sample heating.

Comparison of ETA experimental data and model curves

In Figs 4a and b the experimental ETA data of the perovskite ceramics samples are compared with the respective model curves. A good agreement between the results of modeling and experimental ETA results was achieved.

Figure 5 depicts the temperature dependences of the Ψ(T) functions that characterize the annealing of surface and subsurface structure irregularities of the "as-polished" sample as calculated by using Eq. (4). On heating 'as-polished' sample three steps of the annealing of surface and subsurface structure irregularities, serving as radon diffusion paths, were determined. The decrease of the radon release rate in the ranges 280-560, 800-960 and 960-1200°C was ascribed to the annealing of cracks formed by surface polishing and other surface and subsurface structure irregularities such remaining latent pores, respectively. On the contrary, one annealing step was determined by ETA with the 'as-leached' sample in the range of 800-950°C due to microstructure changes in the titania containing altered subsurface of the sample. Figure 6 presents the temperature dependences of the Ψ(T) and dΨ(T)/dT functions that characterize the annealing of surface and subsurface structure irregularities as calculated by from the ETA data of the "as-polished' (curve 1) and "as-leached" sample (curve 2). It was of interest to compare the relative intensity and temperatures of the maximum rate of the microstructure changes for the "as-prepared" and "as-leached" samples that were observed in the range of 800-960°C. The higher intensity of the annealing of structure irregularities was observed with the "as-poished" sample as compared to the "as-leached" sample. It is in agreement with our assumption

that in this sample a higher amount of structure irregularities was available to enhance the densification of the sample subsurface. However, from Fig. 5 it followed that the maximum rate of the annealing took place at the temperature by about 30°C higher with the 'as-polished' than with "as-leached" sample. The model curves presented in Figs 5 and 6 characterized the mobility of radon atoms as influenced by surface and microstructure changes.

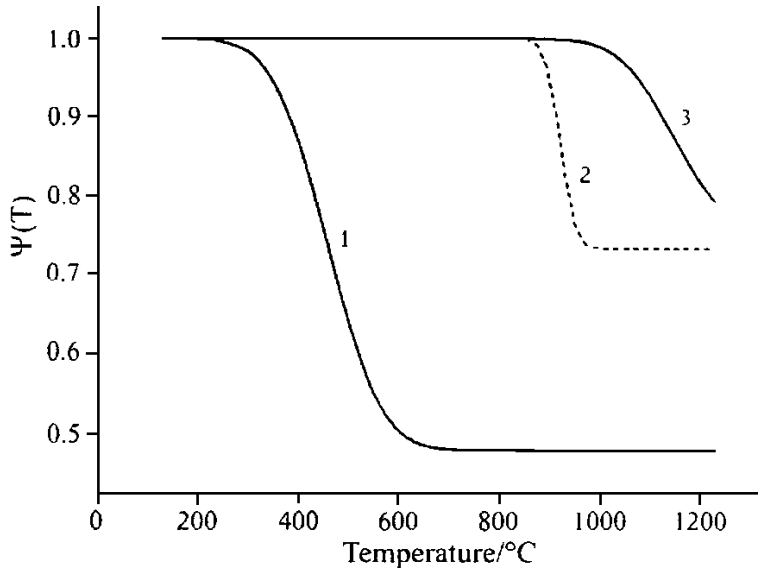

Fig. 5 Temperature dependences of Ψ(T) functions (curves 1, 2 and 3) that characterize the annealing of surface and subsurface structure irregularities during heating of "as-polished" sample

By this way the ETA results made it possible to obtain a supplementary information about annealing of the subsurface of perovskite ceramics before and after leaching. The availability of the ceramics matrix for radon atoms, serving a probe for transport properties (atom size 0.4 nm) can be assessed from the ETA results. Grain boundaries, micropores and others were supposed to serve as channels along which the radon atoms migrated in the ceramic matrix.

Conclusions

The ETA results brought about a supplementary information about the effect of leaching on the microstructure development of perovskite ceramics matrix for encapsulation of hazardous elements. Temperature intervals of the annealing of cracks formed by surface polishing and other surface and subsurface structure irregularities, such as grain boundaries, remaining latent pores, were determined. The ETA results were in agreement with SEM micrographs and XRD patterns used for the surface morphology characterization and phase identification, respectively.

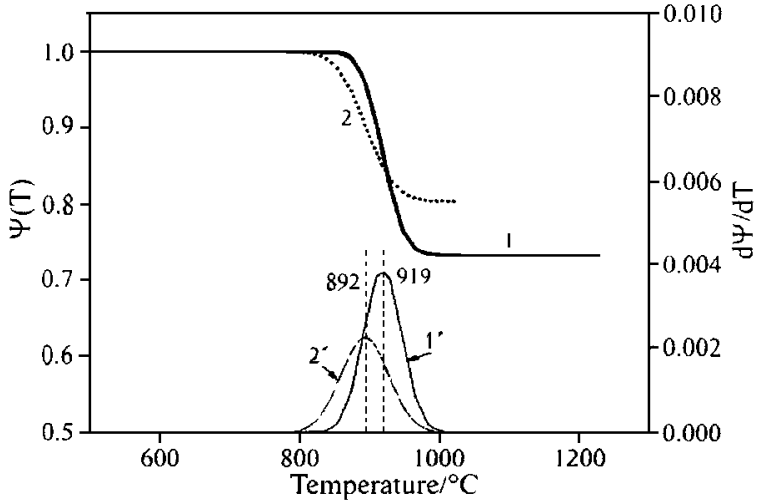

Fig. 6 Comparison of Ψ(T) (curves 1 and 2) and dΨ(T)/dT functions (curves 1' and 2') that characterize the annealing of structure irregularities in the temperature range 80O-960°C for the "as-polished" sample (curves 1 and 1') and "as-leached" sample (curves 2 and 2'), respectively

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References

1. Chemical durability and related properties of solidified high level radioactive waste forms. IAEA Technical report No.257(1985).
2. W. Lutze and R. C Ewing (Eds): Radioactive waste forms for the future, Elsevier Sci. Publishers,

1988.
3. V. Balek, J. Subrt, T. Mitsuhashi, I. N. Beckman and K. Gyoryova, J. Therm. Anal. Cal., 67 (2002) 15.
4. V. Balek and J. Tolgyessy, Emanation thermal analysis and other radiometric emanation methods, in: Wilson and Wilson's Comprehensive Analytical Chemistry, Part XIIC, G. Svehla, Ed.; Elsevier Science Publishers, Amsterdam 1984, p. 304.
5. V. Balek, Thermochim. Acta, 22 (1978) 1.
6. V. Balek and M. E. Brown, Less common techniques, in: Handbook on Thermal analysis and calorimetry, Vol. 1, Chapter 9, Edited by M. E. Brown, Elsevier Science B.V., 1998, p. 445.
7. Nuclear Waste Materials Handbook, Materials Characterization Center, Report DOE/TIC-11499 (1981).
8. I. N. Beckman and V. Balek, J. Therm. Anal. Cal., 67 (2002) 49.
9. F. Kovanda, V. Balek, V. Dornicak, P. Martinec, M. Maslan, L. Bilkova, D. Kolousek and I. M. Bountsewa. J. Therm. Anal. Cal., 71 (2003) 715.
10 V. Balek, N. Todorova, C Trapalis, V. Stengl, E. Vecemikova, J. Subrt, Z. Malek and G. Kordas, J. Therm. Anal. Cal., 80 (2005) 503.
11. N. K. Labhsetwar, V. Balek, S. Rayalu, T. Terasaka, A. Yamazaki, J. Subrt, H. Haneda and T. Mitsuhashi, J. Therm. Anal. Cal., 80 (2005), in print.
12. H. Mitamura, Studies on self-irradiation damage of cerium doped titanate ceramics containing high level nuclear waste, Ph.D. Thesis, Kyoto University, 1997.
13. J. F. Ziegler and J. P. Biersack, The stopping and range of ions in solids, Pergamon Press, New York 1985.