High Temperature Materials, Processes & Diagnostics

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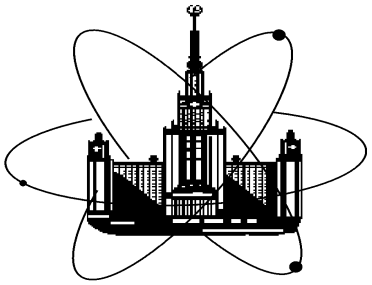


I.N.BECKMAN

Department of Chemistry
M.V.Lomonosov Moscow State University, RF

EMANATION THERMAL ANALYSIS OF PEROVSKITE – BASED CERAMICS

Emanation thermal analysis (ETA) was applied in the investigation of structure transitions in perovskite-based ceramics on heating and cooling. Calcium metatitanate, ($CaTiO_3$) pure and containing admixtures of Al, Ce and Nd (the latter simulating transuranium elements in ceramic form for immobilization of radioactive waste) were investigated by means of ETA. The release of radon-220, formed by the spontaneous α-decay of ^{228}Th and ^{224}Ra and incorporated into samples to maximum depth of 100 nm from the surface due to the recoil, was measured during heating of the samples from 20 to 1200 ^{o}C and subsequent cooling. The effects of mechanical polishing of the ceramics surface, effects of chemical leaching in aggressive media on the ceramics surface, as well as annealing of surface roughness and subsurface microvoids taking place in the samples on heating were characterized by ETA in various gas environments (pure argon and hydrogen containing argon, respectively). The observed effects were evaluated by a new theoretical approach developed for this purpose. This theoretical approach is based on the mathematical description and modeling of radon mobility under dynamic conditions of heat treatment of solids, supposing the presence of structure transitions. A good agreement between theoretical and experimental results was obtained. It was demonstrated that changes in the surface roughness as well microstructure development of ceramic samples subsurface layers can be characterized by means of ETA under *in situ* conditions of heat treatment. The thermal stability of radiation-induced defects in perovskite ceramic powder bombarded by 2.7 MeV He^+ ions or 4 MeV Kr^+ ions to doses of $10^{14} – 10^{16}$ ions/cm^2 was determined by means of ETA. From the ETA results it followed that the perovskite-based ceramics possesses good thermal stability and chemical durability to be used as the ceramic form for immobilization of high level radioactive waste.

Key words:
Perovskite, ceramics, radioactive waste immobilization, emanation thermal analysis, radon

The main advantage of the perovskite based ceramics as the matrix for the high level radioactive waste (HLW) immobilization consists in the high absorption ability for transuranium elements and chemical durability.

Objective

To demonstrate the thoron emanation thermal analysis (ETA) as a method by which the further information about the microstructure of the near surface layers of perovskite-based ceramics can be obtained.

Methods used

Emanation thermal analysis (ETA)
Scanning electron microscopy (SEM)
X-ray diffraction (XRD)
The leaching characteristics of the waste forms were examined according to the MCC-1 test method.

Materials investigated

Calcium metatitanate, ($CaTiO_3$) pure and containing admixtures of Al, Ce and Nd (the latter simulating transuranium elements in ceramic form for immobilization of radioactive waste) were investigated. The nominal chemical composition of the perovskite samples is ascribed by the following formula:

$Ca_{0.98214}$ ($Nd_{0.00790}$ $Ce_{0.00996}$)$Al_{0.01786}$ $Ti_{0.98214O3}$,

where Nd and Ce were used as simulant for Cm and Pu, respectively.
Samples approximately 1x1x0,2 cm in size were irradiated by 2,7 MeV He^+ or 4 MeV Kr^+ ions to doses of $10^{14} – 10^{15}$ ions/cm^2, over circular areas 0,7 cm in diameter.

Altered perovskite ceramics resulting after the MCC-1 leach test was investigated. The virgin "polished" ceramic sample was investigated for comparison. A virgin perovskite sample in a cylinder form (2 cm in diameter and 1 cm high) was prepared by hot pressing at 1250°C/29 MPa for 2 hours. A thin half disk of the ceramic sample was subjected to the MCC-1 leach test in pH=2 buffer solution (0.05M KCl + 0.013M HCl) at 90°C for two months over four 7-day leach periods and a 28-day leach period**.**

EXPERIMENTAL

Emanation thermal analysis (ETA)

The ETA involves the measurement of the release of ^{220}Rn (thoron, half-life, 55,6 s), which was formed by the spontaneous α-decay of ^{228}Th (1,91 years) and ^{224}Ra (3,64 day) according to the following scheme

$$^{228}Th \xrightarrow{\alpha} {}^{224}Ra \xrightarrow{\alpha} {}^{220}Rn \xrightarrow{\alpha}$$

and incorporated into samples to depth of approximately 80 nm from the surface due to the recoil.
The ETA apparatus constructed at the MSU (see Fig.1) was used. The sample subjected to an ETA measurement was placed into a corundum crucible and heated at the constant heating rate of 5 K/min. A constant flow (flow rate 50 ml/min) of gas carried the radon released from the sample into the measuring chamber. Argon, air or argon containing 6% hydrogen were used in the ETA perovckite.

For ETA measurements the samples were labeled using adsorption of radionuclides of ^{228}Th and ^{224}Ra from acetone solution on the sample surface. The specific activity of the sample was 10^5 Bq/g.
The microstructure changes taking place in the near surface layers (up to the depth of approximately 80 nm) of leached perovskite ceramics characterized by ETA under in situ conditions of their heat treatments from 20 to 1200 °C.
The variation in the radon release rate E reflected a densification of the structure, closing pores and/or the alteration in the surface area of the interfaces. Radon atoms were serving as a probe of the microstructure changes in the near surface layers of the labeled ceramic samples.

Model ETA

The radon atoms can be directly released by recoil or trapped at the lattice defects, vacancy clusters, grain boundaries and pores. The defects in the solids can serve both as traps and diffusion paths for radon. As it follows from theories of diffusion and recoil processes, the radon release rate depends on the surface area of the solid-gas interfaces, and on the radon diffusion parameters in the solids matrix.

In the ETA the release of radon atoms (previously incorporated into the solid sample investigated) is measured, serving as a probe of microstructure changes and permeability of the samples towards radon (atom size approximately 0.4 nm). The increase in the radon release rate (E) indicates an opening of the structure and/or the increase of the surface area of the interfaces, whereas the decrease in E reflects a densifications of the structure, closing pores and/or the decrease in the surface area of interfaces.

A mathematical model was used for the evaluation of the experimental data of radon release from the both "as polished" and "as leached" perovskite samples.
By means of the *mathematical model* theoretical ETA curves of the altered and virgin perovskite ceramics, respectively, were calculated. The model is based on the assumption that two independent diffusion paths for radon exist and the radon release by recoil takes place. In the modeling we considered the release rate E of radon as a probability of the release of radon atoms, formed by radioactive alpha - decay of the parent nuclide. The general formula for E was proposed:

$$E = A_0 \cdot \Psi(T) \cdot M(T)$$

where A_0 is a constant, $\Psi(T)$ is the formula describing changes of the surface area upon sample heating, T is the temperature. An integral Gauss function was used to express $\Psi(T)$ as an S-like curve,

describing the decrease of the surface area from an upper limit value to a lower limit value. Hence, we can write:

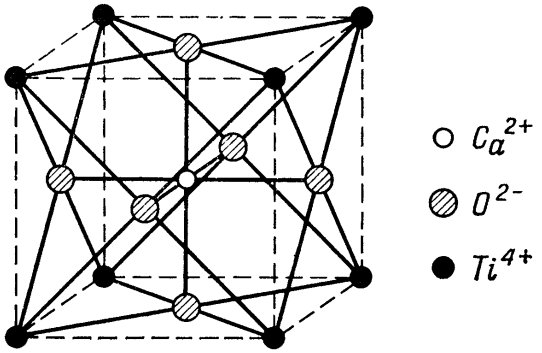
$$\Psi(T) = 1 - 0.5 \cdot [1 + erf(z)]$$

where $z = (T-Tm)/(\sigma^* \sqrt{2})$, $\Delta T = 3\sigma$; Tm - is the temperature corresponding to the maximum rate of surface area change, T is the temperature range in which the surface area change takes place.
The function $M(T)$ can be expressed as follows:

$$M(T) = F \cdot \exp(-Q/2RT)$$

where F is a constant comprising the pre-exponential factor of the temperature dependence of radon diffusion coefficient, Q is the activation energy of radon diffusion, R is the molar gas constant, T is the temperature.

A good agreement was found between the experimental REM data and REM theoretical curve obtained as the result of the modeling.



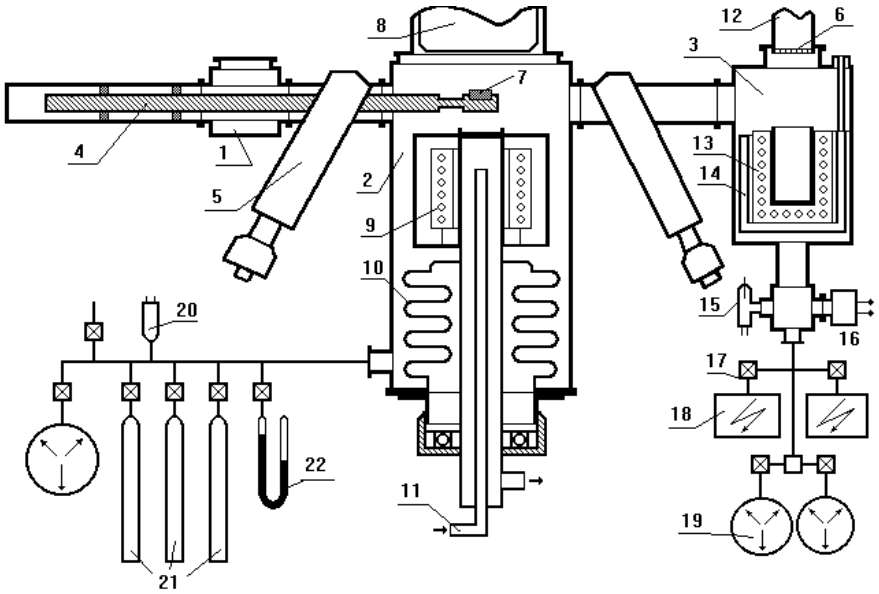


Fig.1 Block diagram of an vacuum experiment plant for introduction inert gases in solids and studying the of radioactive and stable gas release: 1 - chamber for load of specimens, 2- saturation chamber, 3- outgassing chamber, 4- manipulator, 5-free-flow valve, 6-beryllium window, 7-studied sample, 8 - ion gun and device for glow discharge, 9- device for sample heating and temperature control (temperature range from -100 to +1000oC), 10-silfon, 11-device for introducing liquid nitrogen vapor, 12-gamma-radiation source or device for sample deformation, 13-device for sample heating and temperature control (temperature range from -150 to +1500oC), 14-vessel with liquid nitrogen, 15 - mass-spectrometer, 16 - -particles detector, 17-vacuum valve, 18-sputter ion pump, 19-adsorption pump, 20-high vacuum gauge, 21-noble gases cylinders, 22-Hg-gauge.

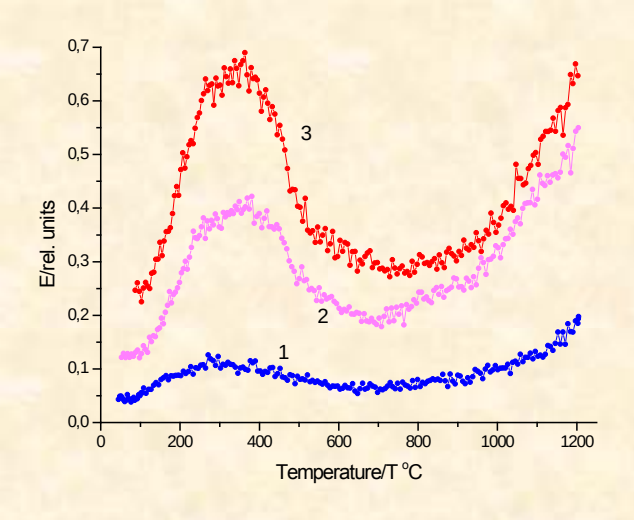


Fig. 2. ETA Perovskite, $CaTiO_3$, bombarded 4 MeV krypton ions, linear heating, argon: 1 – initial $CaTiO_3$; 2 – $CaTiO_3$ irradiated by Kr^+ (10^{14} ion/см$^{-2}$); 3 - $CaTiO_3$ irradiated by Kr+ (10^{15} ion/см$^{-2}$).

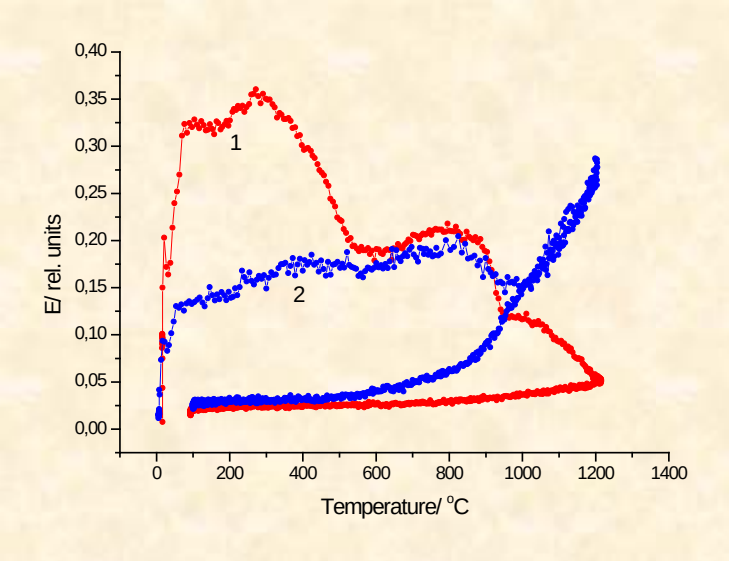


Fig. 3. ETA curves of initial and leaching ceramics: 1 – initial $Ca_{0.98214}$ ($Nd_{0.00790}$ $Ce_{0.00996}$)$Al_{0.01786}$ $Ti_{0.98214O3}$ – as prepared sample; 2 – sample after hydrothermal treatment at 90°C.

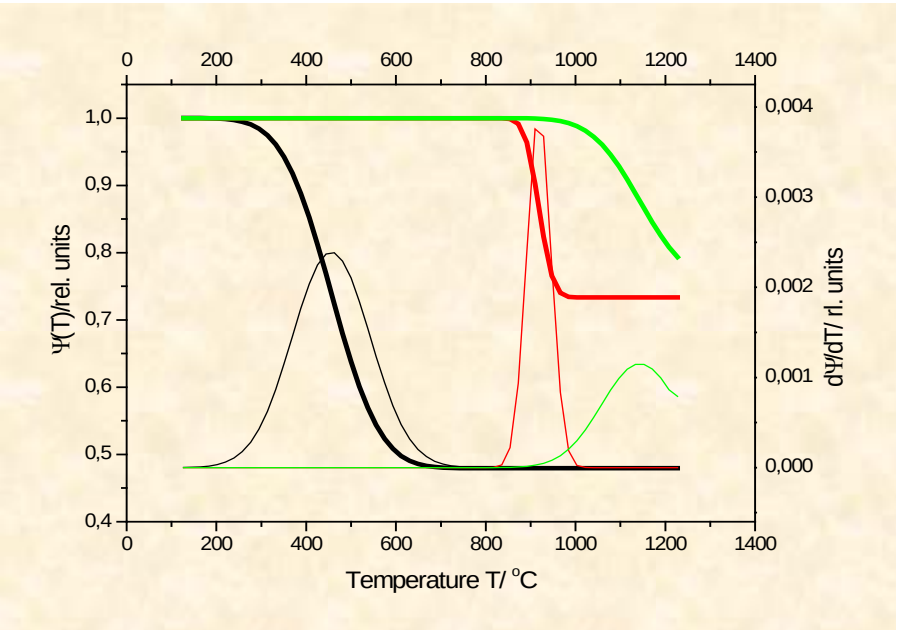


Fig. 4. The structural functions, $\Psi(T)$ and $d\ \Psi/dT$, designed from ETA

The activation energy of radon-220 migration in the near surface layers of the virgin and altered perovskite

	Sample	Atmosphere of ETA	$D_0 1$, $cm^2\backslash s$	Q_D, kJ/mol	$D_0 2$ $cm^2\backslash s$	QD2, kJ/mol	$T_m 1$, ^oC	$\Delta T1$, ^oC	$T_m 2$, ^oC	$\Delta T2$, ^oC	$T_m 3$, ^oC	$\Delta T 3$, ^oC
1	$CaTiO_3$, NP plate	Argon	$7.6*10^{-9}$	42.6	$9.0*10^{-10}$	99.7	533	430.8	–	–	–	–
2	$CaTiO_3$, NP plate bombarded by 10^{14} Kr	Argon	$4.6*10^{-6}$	62.2	$1.5*10^{-8}$	106.4	518	194.4	–	–	–	–
3	$CaTiO_3$, NP plate bombarded by 10^{15} Kr	Argon	$3.5*10^{-6}$	67.2	$5.2*10^{-8}$	148.3	487	159.5	–	–	–	–
4	$Ca_{0.98214}(Nd_{0.00790}Ce_{0.00996})Al_{0.01786}Ti_{0.98214O3}$	Argon +6%H_2	$1.6*10^{-6}$	47.7	–	–	458	214	922	73	1140	204
5	Ceramics №4 (plate), after the MCC-1 leaching test	Argon +6%H_2	$1.5*10^{-6}$	58.6	–	–	–	–	894	87	–	–

where NP - the virgin “non-polished” ceramic sample,
P - the “polished” ceramic sample.