DIFFUSION STRUCTURAL ANALYSIS OF PEROVSKITE CERAMICS PREPARED FROM SOL GEL PRECURSORS

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Diffusion structural analysis (DSA), consisting in the measurement of the release of radon atoms was used with the aim to characterize microstructure changes during heating of bulk perovskite ceramics designed as the matrix for immobilization of high level radioactive waste. A bulk perovskite sample was prepared from the sol-gel precursors by hot pressing at the temperature of 1250 °C/ 29 MPa for 2 hours. The nominal chemical composition of the perovskite samples is $Ca_{0.98214}(Nd_{0.00790} Ce_{0.00996})Al_{0.01786} Ti_{0.98214}O_3$, where Nd and Ce were used as simulant for Cm and Pu, respectively. The chemical durability of the ceramic matrix was determined by leach test following the MCC-l protocol. The "as polished" (virgin) and "as-leached" (altered) samples were characterized by means of DSA measurements during heating in argon + 10% hydrogen up to 1300 °C. Annealing of polishing defects in the "as-polished" perovskite was revealed in the temperature range of 300 - 560°C by the decrease of radon release rate. The decrease of the radon release rate in the range of 880 - 1200°C corresponded to the densification of the samples due to annealing of remaining latent pores. In the altered perovskite sample the decrease of the radon release rate in the range of 800-1000°C indicated the anatase - rutile phase transition. A mathematical model was developed and used for the evaluation of the DSA results.
Key words: Diffusion structure analysis (DSA), perovskite ceramics, high-level radioactive waste immobilization, sol-gel.

1. Introduction

Diffusion structural analysis (DSA) [1, 2], consisting in the measurement of the release of radon atoms was used with the aim to characterize microstructure changes during heating of bulk perovskite ceramics designed as the matrix for immobilization of high level radioactive waste. The perovskite based ceramics was prepared from the sol-gel precursors using tetraisopropyl titanate $(Ti(C_3H_7O)_4)$ and aluminium sec-butoxide $(Al(C_4H_9O)_3)$. Calcium hydroxide as well as small amounts of neodymium and cerium, simulating the transuranium elements, were added into the slurry after hydrolysis of alcoxides so that the nominal chemical composition of the perovskite samples was $Ca_{0.98214}(Nd_{0.00790} Ce_{0.00996})Al_{0.01786} Ti_{0.98214}O_3$.

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.

The internationally recommended testing procedures such as Materials Characterization Center (MCC) [3] leach tests were used in testing chemical durability HLW forms. Thermal stability of initial and leached perovskite ceramics was determined from the DSA results.

2. Experimental

2.1 Preparation of the perovskite ceramics samples [4]

A predetermined excess of methanol was added to a mixture of tetraisopropyl titanate $(Ti(C_3H_7O)_4)$ and aluminium sec-butoxide$(Al(C_4H_9O)_3)$. Water in excess of that required for complete hydrolysis of the methoxide mixture was slowly added to form coagulates. Room temperature slurrying for ~8 h eliminates flocculent aggregates and results in a suspension resembling white paint. Evaporation of alcohol by heating on a hot plate (~120 °C) for ~6 h reduces the volume by about 2/3. Restoration to approximately the original volume by the addition of water. Addition of calcium hydroxide and of neodymium and cerium simulating the transuranium elements in proportions appropriate to its formulation followed by mixing at room temperature for more than 1h and heating the slurry on a hot plate (140° - 150 °C) for ~5 h to reduce its volume until it has the consistency of thick cream.

This approach yields a precursor which is chemically homogenous at sub-micron levels and has an as-dried surface area of > 250 $m^2 \cdot g^{-1}$. Even though small balls of briquette were formed after drying of the mixture of the hydroxide-route precursor and HLW, they were changed to fine powder after calcination.

A bulk perovskite sample was prepared by hot pressing at the temperature of 1250°C / 29 MPa for 2 hours. The nominal chemical composition of the perovskite samples is $Ca_{0.98214}(Nd_{0.00790}Ce_{0.00996})Al_{0.01786}Ti_{0.98214}O_3$, where Nd and Ce were used as simulant for Cm and Pu, respectively. The Nd and Ce rare earth elements were assumed to be trivalent and to be incorporated in the Ca site via an Al^{3+} substitution on a Ti^{4+} site.

2.2 Testing of the chemical durability

The ceramics samples were subjected to the leach test according to the MCC-1 protocol in a pH=2 buffer solution (0.05M KCl + 0.013M HCl) at 90°C for 2 months over four 7-day leach periods and a 28-day leach period.

The dissolution of perovskite is supposed to proceed according to the following scheme:
$$CaTiO_3 + 2H^+ \longrightarrow Ca^{2+} + TiO_2 \text{ (anatase)} + H_2O$$

2.3 Testing of thermal durability

The diffusion structure analysis was used in order to characterize microstructure changes of the ceramics samples submitted to thermal treatments before and after the leach test according to the MCC-1 protocol.
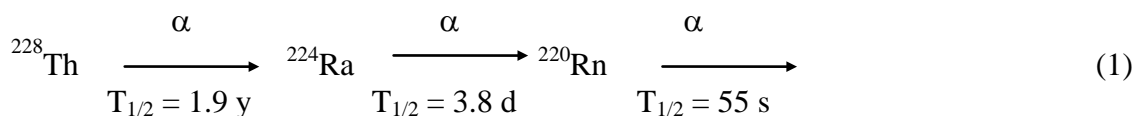
2.4 Diffusion structure analysis (DSA)

Diffusion structural analysis [1, 2] is based on the measurements of the release of inert (radioactive) gases from solid samples. The release of inert gases (in most cases previously incorporated into the samples to be investigated) makes it possible to monitor changes of gels structure and morphology, in the roughness of surfaces and microstructure of the near surface layers of solid samples at „in situ" conditions of their treatment. This method gives an insight into the kinetics of the alteration (ageing) of gels [5] as well degradation of materials surfaces due to thermal or mechanical treatments, chemical interactions or radiation damage. In all cases inert gas atoms serve as *nanostructure probe* of the materials surfaces and surface layers.

2.4.1 Labeling of samples for DSA measurements

Most of the solids to be investigated by DSA do not naturally contain inert gas and it is necessary to label them with a trace amount of the inert gas. Various techniques can be used for the introduction of the inert gas atoms into the samples to be investigated [2,3]. The "as polished" (virgin) and "as-leached" (altered) samples were labeled for the DSA measurements using [228]Th and [224]Ra in the acetone solution.

Trace amounts of thorium [228]Th were adsorbed from aceton solution on the surface of the sample. [220]Rn is formed by spontaneous alpha decay according to the scheme

$$^{228}\text{Th} \xrightarrow{\alpha} {}^{224}\text{Ra} \xrightarrow{\alpha} {}^{220}\text{Rn} \xrightarrow{\alpha} \qquad (1)$$
$$T_{1/2} = 1.9 \text{ y} \qquad T_{1/2} = 3.8 \text{ d} \qquad T_{1/2} = 55 \text{ s}$$

and is introduced into the near surface layers of the sample owing to the recoil energy (85 keV per atom). In perovskite the radon atom penetrate 118 nm. The value of the penetration depth was determined using the TRIM code [5].

During the DSA measurement, the carrier gas (air, nitrogen or another gas) carries the inert gas released by the sample situated in a furnace in the reaction vessels into a detector for the inert gas. The term emanating rate E, has been used to express the release of radon from the sample. It is defined as the ratio of the rate of gas release to the rate of gas formation in the solid. It is determined experimentally 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 γ radioactivity of the labeled 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 α – and γ-radioactivity measurements, respectively. The schematic drawing of the DSA equipment is given in [3].

For the evaluation of DSA results it is supposed that the solubility of inert gas atoms, such as radon, in inorganic solids is negligible and that the inert gases are trapped at lattice defects such as vacancy clusters, grain boundaries and pores. The defects in the solids can serve both as traps and as diffusion paths for the inert gas. A survey of the influence of various factors on the migration of inert gases in solids is given in ref. [2].

In instances when the parent nuclides of the inert gas are incorporated into the solid samples as a quasi-permanent source of the inert gas, the recoil mechanism and diffusion of the radon should be taken into account when evaluating the results of DSA.

Results and discussion
Characterization of perovskite ceramics and its alteration products

Figure 1 presents the results of the diffusion structure analysis of preovskite ceramics obtained during heating and subsequent cooling in argon + 10% hydrogen up to 1300 °C.
Annealing of polishing defects in the "as-polished" sample was revealed by the decrease of radon release rate in the temperature range of 300-560 °C. The decrease of the radon release rate in the range of 880-1200 °C corresponded to the densification of the samples due to annealing of remaining latent pores.(see Fig l, curve 1) The DSA results measured during sample cooling characterized the radon diffusion properties in the perovskite sample heated to 1200 °C in argon containing 6 % of hydrogen.

According to the SEM micrographs (see Fig. 2) the "as-polished" sample microcracks due to polishing were observed on the sample surface. The "as leached" perovskite sample a grain size of 0.2 μm for the crystallites forming the surface layer was determined. From the XRD patterns (see Fig. 3) of the respective perovskite ceramics samples titanium dioxide (anatase) was formed on the sample surface as the results of the leaching. The results of SEM and XRD are in a good agreement with the DSA curves.

The thickness of the altered anatase containing layer was estimated [4] (using the amount of Ca in the leachate) to be approx. 40 μm, the near surface part of the altered layer being labeled by radon atoms for the DSA measurements. From the radon release rate measured during sample heating we can conclude that the polishing defects observed in the "as-polished" samples were eliminated in the course of the hydrothermal treatment. The decrease of the radon release rate in the temperature range of 800-1000 °C indicated the anatase - rutile phase transition. The DSA results of the "as-leached" sample implies that the annealing of remaining latent pores takes place on heating above 1000 °C.

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*** simulated DSA 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:

$$E = A_0 \cdot S(T) \cdot \Psi(T) \qquad (2)$$

where A_0 is a constant, S(T) is the formula describing changes of the changes of the structure irregularities serving as paths for the radon migration on sample heating, T is the temperature. An integral Gauss function was used to express S(T) as an S-like curve. Hence, we can write:

$$S(T) = 1 - 0.5[1 + erf(z)] \qquad (3)$$

where $z = (T-T_m)/ \sigma(2)^{1/2}$, $\sigma = \Delta T/3$; T_m - is the temperature corresponding to the maximum rate of surface area change, ΔT is the temperature range in which the surface area change takes place.
The function M(T) can be expressed as follows:

$$\Psi(T) = F \exp(-Q/2\mathbf{R}T) \qquad (4)$$

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 DSA data and simulated DSA curve obtained as the result of the modeling (see Figs. 4-1 and 4-2). Two independent annealing processes were considered to take place in the near surface layers of leached perovskite ceramics, namely in the temperature 340–600 and 600–980 °C, respectively (Fig. 4-2). The exponential increase of radon release rate obeying the Arhenius law was used for description of the diffusion behavior of radon in altered perovskite after heat treatment from 1000 - 1200 °C. The values of activation energy of radon migration in the near surface layers of the virgin and altered perovskite calculated for the above temperature ranges using the proposed mathematical model are listed in Table 1. It is obvious that the DSA results gave supplementary information about annealing of the near surface layers of the perovskite ceramics before and after leach test following MCC-1 protocol and about the migration of radon atoms in the perovskite matrix for TRU immobilization. Moreover the results of DSA enabled us to assess the availability of the ceramic matrix for radon atoms, serving a noble gas probe (atom size 0.4nm). Grain boundaries, micropores and others are supposed to served as channels along which the radon atoms can migrate in the ceramic matrix.

Conclusions

It was demonstrated that the diffusion structure analysis can be advantageously used to test the thermal stability of the near surface layers of the virgin (as polished) altered (as leached) samples of perovskite ceramics. The ^{220}Rn nuclide was introduced into the near surface layers of the samples due to the recoil energy, serving as the nanoscale probe of the microstructure changes. The mathematical model used for the evaluation of the DSA results confirmed a good agreement with the experimental data characterizing the microstructure development during sample heating in argon + 10% hydrogen up to 1300 °C. The parameters used in the model for the description of the radon release rate enabled us to compare intensity of the development of the surface area and structure irregularities serving for the radon migration in the samples investigated.

References

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Table 1. Activation energy of radon migration in the near surface layers of altered and virgin perovskite ceramics.

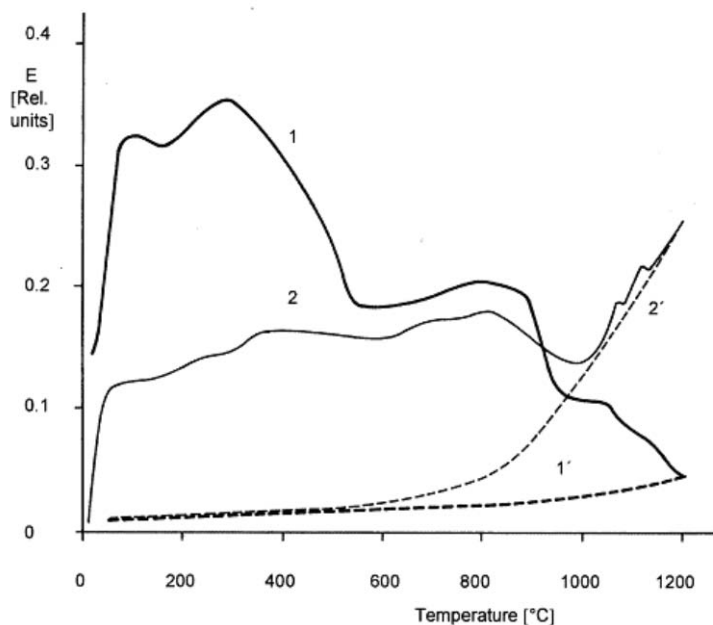| Virgin perovskite sample		Altered perovskite sample	
Temperature range [°C]	Activation energy [kJ•mol^{-1}]	Temperature range [°C]	Activation energy [kJ•mol^{-1}]
Heating run 340 – 600	28.04	Heating run 340 – 600	6.34
600 – 980	10.24	600 – 980	18.61
980 – 1200	60.29	980 – 1200	91.64
Cooling run 400 – 1200	129.00	Cooling run 400 – 1200	126.00

Captions to Figures

Fig. 1 DSA results of bulk perovskite hot pressed sample prepared at JAERI during heating and subsequent cooling in argon + 6% hydrogen. Curve 1 – as polished sample, curve 2 – as leached sample (after hydrothermal treatment at 90 °C). Curve 1' and 2'' were measured during cooling of the respective samples.
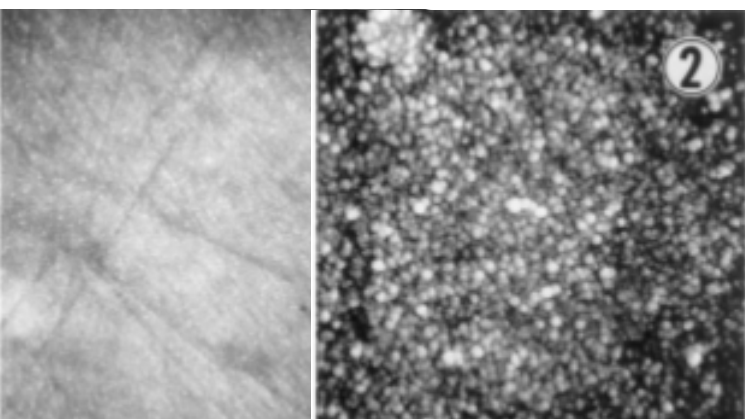
Fig. 2 SEM micrographs of perovskite samples (1) polished surface of the virgin sample, (2) altered surface.

Fig. 3 X-ray diffraction patterns of „as-polished" and „as-leached" perovskite ceramic samples. The signs of A, P, and * stand for anatase, perovskite and unidentified.
Fig. 4-1 Comparison of experimental (points) and simulated (full lines) DSA curves describing thermal behavior of virgin perovskite ceramics sample.
Fig. 4-2 Comparison of experimental (points) and simulated (full lines) DSA curves describing thermal behavior of altered perovskite ceramics sample.

Fig. 1 DSA results of bulk perovskite hot pressed sample prepared at JAERI during heating and subsequent cooling in argon + 6% hydrogen. Curve 1 – as polished sample, curve 2 – as leached sample (after hydrothermal treatment at 90 °C). Curve 1' and 2'' were measured during cooling of the respective samples.

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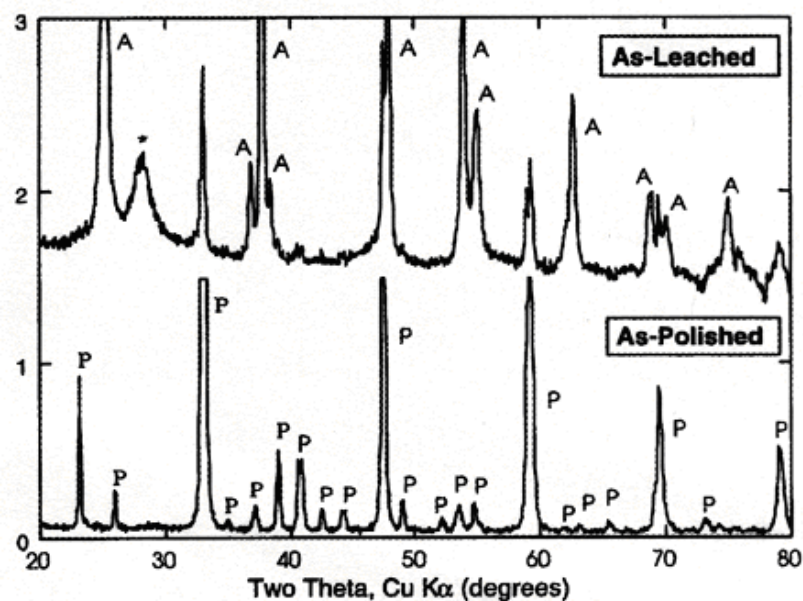

Fig. 3 X-ray diffraction patterns of „as-polished" and „as-leached" perovskite ceramic samples. The signs of A, P, and * stand for anatase, perovskite and unidentified.
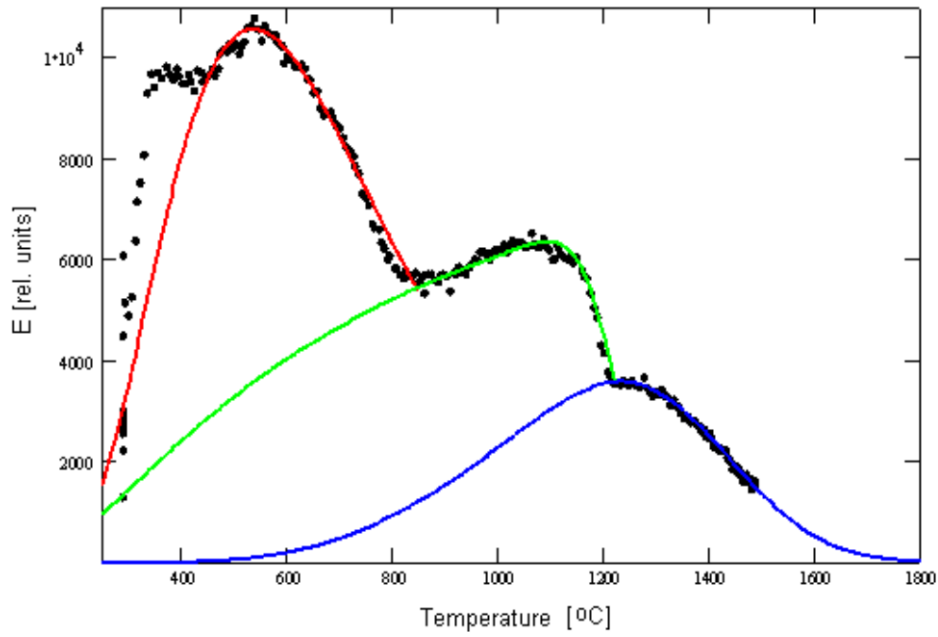
Fig. 4-1 Comparison of experimental (points) and simulated (full lines) DSA curves describing thermal behavior of virgin perovskite ceramics sample.
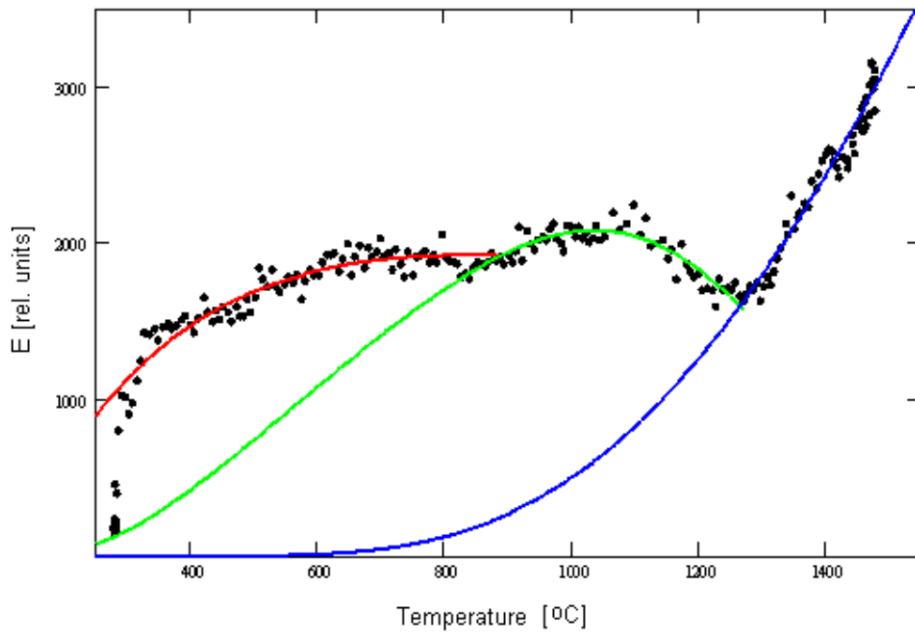

Fig. 4-2 Comparison of experimental (points) and simulated (full lines) DSA curves describing thermal behavior of altered perovskite ceramics sample.