High-temperature radiolysis of modified lithium orthosilicate pebbles with additions of titanium dioxide

A. Zarins\textsuperscript{a}, G. Kizane\textsuperscript{a}, A. Supe\textsuperscript{a}, R. Knitter\textsuperscript{b}, M. H.H. Kolb\textsuperscript{b}, O. Leys\textsuperscript{b}, L. Bauman\textsuperscript{a,c}, D. Conka\textsuperscript{a} and O. Valtenbergs\textsuperscript{a}.

\textsuperscript{a}University of Latvia, Institute of Chemical Physics, 4 Kronvalda blvd., LV-1010, Riga, Latvia. 
\textsuperscript{b}Karlsruhe Institute of Technology, Institute for Applied Materials (IAM-WPT), 76021, Karlsruhe, Germany.
\textsuperscript{c}Latvian Institute of Organic Synthesis, 21 Aizkraukles str., LV-1006, Riga, Latvia.

E-mail contact of main author: arturs.zarins@lu.lv

Abstract. Lithium orthosilicate (Li$_2$SiO$_4$) pebbles with 2.5 wt.% excess of silicon dioxide (SiO$_2$) are the European Union’s designated reference tritium breeding ceramics for the Helium Cooled Pebble Bed (HCPB) Test Blanket Module (TBM). However, the latest irradiation experiments showed that the reference Li$_2$SiO$_4$ pebbles may crack and form fragments under operation conditions as expected in the HCPB TBM. Therefore, it has been suggested to change the chemical composition of the reference pebbles and to replace the excess of SiO$_2$ by titanium dioxide (TiO$_2$), to obtain lithium metatitanate (Li$_2$TiO$_3$) as a second phase. The aim of this research was to investigate the high-temperature radiolysis of the modified Li$_2$SiO$_4$ pebbles with different contents of TiO$_2$ for the first time. The high-temperature radiolysis was performed with accelerated electrons by a linear electron accelerator ELU-4 (E=5 MeV) up to 5 Gy absorbed dose at 380-670 K in dry argon atmosphere. The formation of radiation-induced defects and radiolysis products was analyzed by electron spin resonance spectroscopy. The phase transitions were detected by powder X-ray diffractometry and Fourier transform infrared spectroscopy. The microstructural changes were investigated by scanning electron microscopy. Obtained results indicates that the modified Li$_2$SiO$_4$ pebbles with additions of TiO$_2$ have slightly higher radiation stability compared with the reference pebbles and the thus have potential to be used as a tritium breeding ceramic.

1. Introduction

In the International Thermonuclear Experimental Reactor (ITER, Cadarache, France) several concepts of Test Blanket Modules (TBM) will be tested and verified, because the tritium breeding is a key issue in future burning plasma machines, like DEMO (Demonstration fusion reactor) [1, 2]. The Helium Cooled Pebble Bed (HCPB) TBM, proposed by the European Union, will use lithium orthosilicate (Li$_2$SiO$_4$) pebbles with 2.5 wt.% excess of silicon dioxide (SiO$_2$) as reference tritium breeding ceramic [1-3]. Due to the excess of SiO$_2$, the reference pebbles have two phases – 90 mol\% Li$_2$SiO$_4$ and 10 mol\% lithium metasilicate (Li$_2$SiO$_3$) [4, 5].

The reference Li$_2$SiO$_4$ pebbles have appropriate properties for the tritium breeding, i.e. a high lithium density ($\rho_{Li}=0.54$ g cm$^{-3}$) and melting point (T=1523 K), a good tritium release behaviour and chemical compatibility with structural materials. However, beside the main task to produce and release tritium, the reference pebbles also must be able to withstand the harsh conditions as expected during exploitation [1, 2].

The latest irradiation experiments [6] showed that the reference Li$_2$SiO$_4$ pebbles will likely perform sufficiently in HCPB TBM. However, it has been also observed that the reference pebbles may crack and form fragments during irradiation. Therefore, it has been suggested to increase mechanical stability of the pebbles, to withstand operation conditions as expected in the HCPB TBM.

One possible option to increase the mechanical stability of the tritium breeding ceramic is to change the chemical composition of the reference Li$_2$SiO$_4$ pebbles and to replace the excess of SiO$_2$ by titanium dioxide (TiO$_2$) [7]. Due to the additions of TiO$_2$, lithium metatitanate (Li$_2$TiO$_3$) as a secondary phase is obtained in the modified Li$_2$SiO$_4$ pebbles. The Li$_2$TiO$_3$ is also approved as “back-up” solution for the
tritium breeding in the HCPB TBM, due to the good tritium release behaviour and appropriate mechanical, thermal and chemical properties [3]. Therefore, in combining these two phases – Li$_2$SiO$_4$ and Li$_2$TiO$_3$, it is anticipated to obtain a modified tritium breeding ceramic with improved mechanical properties, without losing the benefit of the high lithium density and good tritium release behaviour.

However, to develop a new chemical composition for the tritium breeding ceramic, it is a critical issue to understand the high-temperature radiolysis, i.e. radiation-induced chemical processes, microstructural changes and phase transitions, which will occur during irradiation at elevated temperature. From previous studies [8-15], it is known that the formation, accumulation and annihilation of radiation-induced defects (RD) and radiolysis products (RP) may occur in the tritium breeding ceramic. Such RD and RP will induce changes of thermal and mechanical properties, swelling and degradation of mechanical integrity, and may also affect the tritium diffusion and release process.

The aim of this research was to investigate the high-temperature radiolysis of the modified Li$_2$SiO$_4$ pebbles with different contents of TiO$_2$ for the first time, in order to estimate radiation stability.

2. Experimental

2.1. Fabrication of ceramic specimens

The three types of the modified Li$_2$SiO$_4$ pebbles with different contents of TiO$_2$ (screened to 650-900 μm) were selected for investigation together with the reference pebbles (Table 1). Both, the reference and modified Li$_2$SiO$_4$ pebbles were produced by an enhanced melting process at Karlsruhe Institute of Technology (Germany) [3, 16, 17]. To achieve a homogenous microstructure, the fabricated pebbles were annealed at 1220 K for 504 h in air.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reference pebbles</th>
<th>Modified pebbles No. 1</th>
<th>Modified pebbles No. 2</th>
<th>Modified pebbles No. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical composition</td>
<td>90 mol% Li$_2$SiO$_4$</td>
<td>90 mol% Li$_2$SiO$_4$</td>
<td>80 mol% Li$_2$SiO$_4$</td>
<td>70 mol% Li$_2$SiO$_4$</td>
</tr>
<tr>
<td>Minor impurities</td>
<td>10 mol% Li$_2$SiO$_3$</td>
<td>10 mol% Li$_2$TiO$_3$</td>
<td>20 mol% Li$_2$TiO$_3$</td>
<td>30 mol% Li$_2$TiO$_3$</td>
</tr>
<tr>
<td>n.d.$^2$</td>
<td></td>
<td>Pt Ca, Al, Mg, Fe</td>
<td>Pt</td>
<td></td>
</tr>
</tbody>
</table>

$^1$detected by X-ray fluorescence spectroscopy  
$^2$n.d. – Not detected, i.e. below detection limit

2.2. Preparation and irradiation of samples

The reference and modified Li$_2$SiO$_4$ pebbles were encapsulated in quartz tubes with dry argon and were irradiated by a linear electrons accelerator ELU-4 (E=5 MeV, Salaspils, Latvia), up to 5 h per day (Table 2). The high-temperature radiolysis was performed up to 5 GGY absorbed dose at different irradiation temperatures – from 380 to 670 K. Accelerated electron flux was used in this research, as a preliminary approach, to avoid the formation of tritium and other nuclear transitions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Irradiation conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorbed dose, GGY</td>
<td>No. 1 3.5 5</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>380-560 440-670 380-650</td>
</tr>
<tr>
<td>Average temperature, K</td>
<td>460 520 520</td>
</tr>
<tr>
<td>Dose rate, MGy h$^{-1}$</td>
<td>42 56 42</td>
</tr>
</tbody>
</table>

2.3. Methods of characterization

The formation and accumulation of paramagnetic RD and RP in the reference and modified Li$_2$SiO$_4$ pebbles before and after irradiation were analysed by electron spin resonance (ESR) spectroscopy. The
ESR spectra were recorded by a Bruker BioSpin X-band radiospectrometer (300-400 mT, 30 dB, 0.2 mW, 9.83 GHz) operating at 100 kHz field modulation in room temperature.

The phase transitions in the pebbles were detected by qualitative powder X-ray diffractometry (p-XRD) and Fourier transform infrared (FT-IR) spectroscopy. The p-XRD patterns were obtained by a Bruker D8 (10-60° 2θeta, CuKα, 0.15418 nm) and the FT-IR spectra by a Perkin Elmer Spectrum Two (450-4000 cm\(^{-1}\), ±4 cm\(^{-1}\) pressed in KBr pellets, air).

The microstructural changes of the pebbles were investigated at etched cross-section by an Field Emission Scanning Electron Microscopy (FE-SEM, Zeiss, Supra 55).

3. Results and discussion

3.1. Microstructural changes and phase transitions in modified Li\(_4\)SiO\(_4\) pebbles

Using p-XRD it has been observed that the modified Li\(_4\)SiO\(_4\) pebbles with additions of TiO\(_2\) before irradiation have two crystallised phases – a main phase, Li\(_4\)SiO\(_4\), and a secondary phase, Li\(_2\)TiO\(_3\) (Fig. 1). The minor metallic impurities, mostly Pt, within the modified pebbles were detected by X-ray fluorescence spectroscopy (Bruker S8-TIGER). Impurities are most likely formed during the fabrication process, due to the melting in a Pt alloy crucible [3, 16, 17] or are introduced by the raw materials.

![Graph showing ESR spectra](image)

**FIG. 1.** p-XRD patterns of the reference Li\(_4\)SiO\(_4\) pebbles with 10 mol% Li\(_2\)SiO\(_3\) and the modified Li\(_4\)SiO\(_4\) pebbles with 10-30 mol% Li\(_2\)TiO\(_3\) before irradiation.

After irradiation of up to 5 GGy absorbed dose, major changes in the structure of the reference Li\(_4\)SiO\(_4\) pebbles with 10 mol% Li\(_2\)SiO\(_3\) and modified pebbles with 10-30 mol% Li\(_2\)TiO\(_3\) were not observed by p-XRD patterns (Fig. 3) and FT-IR spectra. However, due to the small radiolysis degree of Li\(_4\)SiO\(_4\) and Li\(_2\)TiO\(_3\) major changes were not expected.

![Graph showing ESR spectra](image)

**FIG. 3.** p-XRD patterns of the reference Li\(_4\)SiO\(_4\) pebbles with 10 mol% Li\(_2\)SiO\(_3\) (left) and modified Li\(_4\)SiO\(_4\) pebbles with 10 mol% Li\(_2\)TiO\(_3\) (right) before and after irradiation with accelerated electrons up to 1, 3.5 and 5 GGy absorbed dose at 380-670 K in dry argon atmosphere.

Radiolysis degree is percentage proportion of decomposed molecules or ions versus initial number of molecules or ions before irradiation. Previously J. Tiliks et al. (2003) [12] reported that the radiolysis degree of Li\(_4\)SiO\(_4\) pebbles with 2 wt% SiO\(_2\) is 0.1-1 mol% after irradiation up to 1 GGy absorbed dose,
while for Li$_2$TiO$_3$ pebbles it is only $10^{-3}$ mol% after irradiation to 0.5 GGy. The radiolysis of Li$_4$SiO$_4$ and Li$_2$TiO$_3$ can be described by the summary equations (1) and (2).

\[
\text{Li}_4\text{SiO}_4 \rightarrow 2\text{Li}_2 + \text{Li}_2\text{SiO}_3 + 0.5 \text{O}_2 \quad (1)
\]
\[
\text{Li}_2\text{TiO}_3 \rightarrow 2\text{Li} + \text{TiO}_2 + 0.5 \text{O}_2 \quad (2)
\]

The microstructure of the reference and modified Li$_4$SiO$_4$ pebbles at etched cross-section before and after irradiation with accelerated electrons is shown in Fig. 4. In the reference pebbles before irradiation at etched cross-section Li$_4$SiO$_4$ phase is displayed in dark grey colour with inclusions of smaller, light-grey grains of Li$_2$SiO$_3$. Whereas in the modified pebbles, light-grey grains of Li$_2$TiO$_3$ are very small and homogeneously distributed as inclusions in Li$_4$SiO$_4$ phase, dark-grey.

The microstructure of the reference and modified pebbles is only slightly changed during irradiation with accelerated electrons beside the agglomeration of pores.

<table>
<thead>
<tr>
<th>Before irradiation</th>
<th>After irradiation (D=1 GGy, T=480-560 K, dry argon)</th>
<th>After irradiation (D=3.5 GGy, T=440-670 K, dry argon)</th>
<th>After irradiation (D=5 GGy, T=380-650 K, dry argon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 mol% Li$_4$SiO$_4$</td>
<td>90 mol% Li$_4$SiO$_4$</td>
<td>80 mol% Li$_4$SiO$_4$</td>
<td>70 mol% Li$_4$SiO$_4$</td>
</tr>
<tr>
<td>10 mol% Li$_2$SiO$_3$</td>
<td>10 mol% Li$_2$SiO$_3$</td>
<td>20 mol% Li$_2$TiO$_3$</td>
<td>30 mol% Li$_2$TiO$_3$</td>
</tr>
</tbody>
</table>

**FIG. 4.** Microstructure of the reference Li$_4$SiO$_4$ pebbles with 10 mol% Li$_2$SiO$_3$ and modified Li$_4$SiO$_4$ pebbles with 10-30 mol% Li$_2$TiO$_3$ at etched cross-section before and after irradiation with accelerated electrons up 1, 3.5 and 5 GGy absorbed dose at 380-670 K in dry argon atmosphere

### 3.2. Qualitative analysis of RD and RP in modified Li$_4$SiO$_4$ pebbles

The formation of hole and electron type RD and RP in the reference Li$_4$SiO$_4$ pebbles take place through three main stages [8]. In the first stage of the radiolysis primary electron and hole type RD, like, E’ centres (SiO$_3^{3-}$ or $\equiv \text{Si} \cdot$) and HC$_2$ centres (SiO$_4^{3-}$ or $\equiv \text{Si} - \text{O} - \text{O} \cdot$), are formed. In the second and third stage of radiolysis secondary RD, like, peroxide radicals (\(\equiv \text{Si} - \text{O} - \text{O} \cdot\)) etc., and chemically stable RP, like, molecular oxygen (O$_2$), colloidal lithium (Li$_n$) and silicon (Si$_n$), silanol ($\equiv \text{Si} - \text{Si} \equiv$), disilicate ($\equiv \text{Si} - \text{O} - \text{Si} \equiv$) and peroxide ($\equiv \text{Si} - \text{O} - \text{O} - \text{Si} \equiv$) bonds etc., are generated. The symbol “$\equiv$” represents three back bonds to three oxygen atoms in the crystal structure.

Most crucial are electron type RD and RP, i.e. E’ centres and Li$_n$ particles, which can interact with tritium and may disturb tritium diffusion and decrease its retention. The RD and RP in the Li$_4$SiO$_4$ pebbles can be detected and distinguished by physical methods, like, ESR spectroscopy, thermo-
stimulated luminescence (TSL) and optical spectroscopy etc., and chemical methods, like, lyoluminescence (LL) and the method of chemical scavengers (MSC).

The MSC is based on the difference of red-ox properties of hole and electron type RD and RP in acid containing solvents [18]. Previously, using the MSC it was determined that after irradiation up to 11 GGy absorbed dose at 550–590 K in dry argon, up to 95% of the accumulated electron type RD and RP in the reference Li₂SiO₄ pebbles are L₁₆ particles and aggregates of simple centres. Simple electron centres consist of E’ centres, localized one or two electrons in oxygen vacancies (so called F’ and F° centres) etc. However, due to the small solubility of Li₂TiO₃ phase, the formation of RD and RP in the modified Li₅SiO₄ pebbles were analyzed only by ESR spectroscopy.

The E’ centres, L₁₆ particles and F° centres possess paramagnetic properties and thus could be detected and analysed by ESR spectroscopy. The F’ centres generate a broad ESR signal with hyperfine structure (g=2.0030, ∆H=20 mT), while the E’ centre only forms one characteristic signal (g=2.001, ∆H=1 mT [18]). It has been assumed that the L₁₆ particles localise as particles of two kinds – particles having the size <1 μm (Lorentzian signal, g=2.0025, ∆H≤10² mT) and 1-10 μm (Dysonian signal, g=2.0035, ∆H=10 mT) [12].

The ESR spectra of the reference and modified Li₅SiO₄ pebbles before and after irradiation up to 1 GGy absorbed dose at 380-560 K in dry argon atmosphere are shown in Fig. 5.

![ESR spectra of the reference Li₅SiO₄ pebbles with 10 mol% Li₅SiO₄ (left) and modified Li₅SiO₄ pebbles with 10-30 mol% Li₂TiO₃ (right) before and after irradiation with accelerated electrons up to 1 GGy absorbed dose at 380-560 K in dry argon atmosphere.](image)

In the ESR spectra of the reference Li₅SiO₄ pebbles with 10 mol% Li₂TiO₃ after irradiation the formation of four signal with similar g-factor (from 2.032 to 2.002) were observed (Fig. 5, left). These signals were attributed to the E’ centres (g=2.002±0.003), HC₂ centres (g₁=2.014±0.003 and g₂=2.020±0.003) and probably peroxide radicals (g=2.032±0.003), which have been investigated and characterized in previous experiments [18]. Presumably, the signal of L₁₆ in the ESR spectra cannot be observed due to particle aggregation, and the signal of F° centres is too broad to be analysed.

 Whereas in the ESR spectra of the modified Li₅SiO₄ pebbles with 10-30 mol% Li₂TiO₃ the formation of two main groups of the first derivative signals were detected (Fig. 5, right). The first group consist of five signals with g-factor from 2.037 to 2.004 while the second group from three signals with g-factor from 1.97 to 1.93.

The signals of the first group (g₁=1.996±0.003, g₂=2.004±0.003, g₃=2.012±0.003, g₄=2.015±0.003 and g₅=2.037±0.003) in the ESR spectra of the modified Li₅SiO₄ pebbles are characteristic to the paramagnetic RD and RP, which are formed and accumulated in “pure” lithium silicate [18] and titanate [19] ceramics. Therefore, the ESR signal with a g-factor of 2.004±0.003 might be attributed to E’ centres (SiO₂³⁻/TiO₂³⁻), in contrast to the signals with g-factor 2.012±0.003 and 2.015±0.003, which can be assigned to HC₂ centres (SiO₂⁻/TiO₃⁻). The ESR signal with g-factor 2.037±0.003 probably could be attributed to peroxide radicals (≡Si – O – O·⁻), whereas the broad signal with g-factor 1.996±0.003 may be associated as part of the Dysonian signals of L₁₆ particles.
The second group of signals (g₁=1.97±0.01, g₃=1.95±0.01 and g₃=1.92±0.01) in the ESR spectra of the modified Li₃SiO₄ pebbles is broad, complex and uncharacteristic for the reference pebbles. Previously V. Grismanovs et al. (2000) [19] and P. Lombard et al. (2011) [20] reported the formation of signals with similar g-factor in the Li₂TiO₃ and other alkali titanates after irradiation and related them to Ti³⁺. However, Ti³⁺ ions are not thermally stable and after thermal treatment at 323 K, signals of Ti³⁺ in the ESR spectra practically disappear. Therefore, it has been assumed that these broad, complex and uncharacteristic signals in the modified pebbles also may be assigned to the paramagnetic metallic impurities, for example, Pt³⁺ and Pt⁺ ions [21-23]. Due to that, all of them were entitled as un-identified RD in the following.

3.3. Quantitative analysis of paramagnetic RD and RP in modified Li₃SiO₄ pebbles

To compare the radiation stability of the modified Li₃SiO₄ pebbles with reference pebbles, the concentration of accumulated paramagnetic RD and RP, i.e. E’ centres, HC₂ centres, peroxide radicals and Li₃n particles, were selected as main comparative parameter (Fig. 6). These RD and RP were selected, due to the possible interaction and formation of chemically stable bonds with tritium. Whereas, the concentration of the un-identified RD (g₁=1.97±0.01, g₂=1.95±0.01 and g₃=1.92±0.01) were not further analysed, due to broad, complex and overlapped signals in the ESR spectra.

![Image](https://example.com/image.png)

**FIG. 6.** The concentration of E’ centres (g₁=2.004±0.003), HC₂ centres (g₂=2.012±0.003 and g₃=2.015±0.003), peroxide radicals (g=2.037±0.003) and Li₃n particles (g=1.996±0.003) in the reference Li₃SiO₄ pebbles with 10 mol% Li₃SiO₄ and the modified pebbles with 10-30 mol% Li₂TiO₃ after irradiation with accelerated electrons up to 1 GgY absorbed dose at 380-560 K in dry argon atmosphere.

The Li₂TiO₃ has a smaller decomposition degree and radiation chemical yield of RD and RP than Li₃SiO₄ and Li₃SiO₄ and thus could increase the radiation stability of the modified pebbles. The obtained results clearly confirm this suggestion, and by replacing Li₃SiO₄ with equal molar amounts of Li₂TiO₃ phase in the modified Li₃SiO₄ pebbles, the total concentration of paramagnetic RD and RP decreases (Fig. 6, left). However, the analysis of RD and RP formation as a function of the Li₂TiO₃ content in the modified pebbles requires additional experiments. It was assumed that this effect could be related to several factors, like pebble microstructure, grain size or different contents of metallic impurities etc.

The hole and electron type RD and RP in the reference Li₃SiO₄ pebbles are formed in equivalent amounts. The E’ and HC₂ centres are the primary RD of Li₃SiO₄ and Li₂TiO₃ (Eqs. (3-6)), whereas peroxide radicals are formed in the second or third stage of radiolysis (Eq. (7)). The Li₃n particles forms at the radiolysis of the Li₃SiO₄ and Li₂TiO₃ because of coagulation of the electron type RD.

\[
\begin{align*}
\text{SiO}_4^{4-} & \rightarrow \text{SiO}_4^{3-} \quad (\text{HC}_2 \text{ centre}) + e^- \quad (3) \\
\text{TiO}_2^{3-} & \rightarrow \text{TiO}_2^{2-} \quad (\text{HC}_2 \text{ centre}) + e^- \quad (4) \\
\text{SiO}_4^{4-} + e^- & \rightarrow \text{SiO}_4^{3-} \quad (E' \text{ centre}) + O^2- \quad (5) \\
\text{TiO}_2^{3-} + e^- & \rightarrow \text{TiO}_2^{2-} \quad (E' \text{ centre}) \quad (6) \\
\text{Si}^+ \quad (E' \text{ centre}) + O_2 & \rightarrow \text{Si}-\text{O}-\text{O}^- \quad (7)
\end{align*}
\]

In the reference Li₃SiO₄ pebbles after irradiation up to 1 GgY absorbed dose at 380-670 K mainly E’ centres are accumulated – up to 75 % (Fig. 6, right), most likely due to the elevated irradiation temperature and the high absorbed dose. Whereas the concentration of HC₂ centres and peroxide radicals
is quite small. As well as the concentration of Li, particles must be regarded with suspicion, due to the overlapping of Dysonian signal with other ESR signals and particle aggregation. Replacing Li₂SiO₃ with an equal molar amount of Li₂TiO₃ as a secondary phase in the Li₄SiO₄ pebbles decreases the concentration of E’ centres.

Previously J. Tiliks et al. (1991) reported [8] that the addition of metallic oxides, like iron oxide (Fe₂O₃), lead oxide (PbO₂) and chromium oxide (Cr₂O₃), may decrease the concentration of RD up to 80 %. Therefore it has been assumed that also Pt impurities in the modified Li₄SiO₄ pebbles could be in the most stable Pt⁴⁺ or Pt⁶⁺ form (PtO, PtO₂ or Li₂PtO₃), due to the fabrication conditions, and thus may act as electron scavenger centres (Eqs. (8-11)). Both, Pt⁴⁺ and Pt⁶⁺ do not show an ESR signal and thus could not be detected by ESR spectroscopy before irradiation.

\[
\begin{align*}
\text{Pt}^{4+} + e^- & \leftrightarrow \text{Pt}^{2+} \ (8) \\
\text{Pt}^{3+} + e^- & \leftrightarrow \text{Pt}^{2+} \ (9) \\
\text{Pt}^{2+} + e^- & \leftrightarrow \text{Pt}^{+} \ (10) \\
\text{Pt}^+ + e^- & \leftrightarrow \text{Pt}^{0} \ (11)
\end{align*}
\]

In the presence of Pt impurities, concentration of formed free electrons could be reduced during irradiation and thus the concentration of E’ centres was rapidly decreased. In addition, in these reactions Pt⁺ and Pt³⁺ ions are formed as by-products and thus broad additional signals were detected in the ESR spectra of the modified pebbles at room temperature.

The total concentration of paramagnetic RD and RP in the reference and modified Li₄SiO₄ pebbles after irradiation with different absorbed doses at 380-670 K are shown in Fig. 7. It can be concluded that the modified Li₄SiO₄ pebbles with 10-30 mol% Li₂TiO₃ as a secondary phase have slightly higher radiation stability compared to the reference pebbles. Therefore, the modified pebbles have the potential to combine the advantages of Li₄SiO₄ and Li₂TiO₃ as a tritium breeding ceramic. However, all above mentioned results also clearly confirm the necessity to further study the radiation effects in the modified pebbles, which will occur under the exploitation conditions of the HCPB TBM.

![Graph showing total concentration of paramagnetic RD and RP in reference and modified Li₄SiO₄ pebbles with 10 mol% Li₂SiO₃ and modified pebbles with 10-30 mol% Li₂TiO₃ after irradiation with accelerated electrons with absorbed doses of 1, 3.5 and 5 GGy at 380-670 K in dry argon atmosphere.]

**FIG. 7.** The total concentration of paramagnetic RD and RP in the reference Li₄SiO₄ pebbles with 10 mol% Li₂SiO₃ and modified pebbles with 10-30 mol% Li₂TiO₃ after irradiation with accelerated electrons with absorbed doses of 1, 3.5 and 5 GGy at 380-670 K in dry argon atmosphere.

### 4. Conclusions

In this research the high-temperature radiolysis (accelerated electrons, D=1-5 GGy, T=380-670 K, dry argon) of the modified Li₄SiO₄ pebbles with 10-30 mol% Li₂TiO₃ as a secondary phase was investigated and described for the first time. The obtained results confirm the suggestion that the modified Li₄SiO₄ pebbles with 10-30 mol% Li₂TiO₃ have slightly higher radiation stability in comparison with the reference Li₄SiO₄ pebbles with 10 mol% Li₂SiO₃. Therefore, the modified pebbles have the potential to combine the advantages of Li₄SiO₄ and Li₂TiO₃ as a tritium breeding ceramic for the HCPB TBM.

After irradiation with accelerated electrons up to 5 GGy absorbed dose at 380-670 K, major changes in the microstructure of the modified Li₄SiO₄ pebbles were not observed by p-XRD, SEM and FT-IR spectroscopy. By using ESR spectroscopy it was determined that in the modified pebbles several paramagnetic species of electron and hole type RD and RP are formed and accumulated, like E’ centres (SiO₂³⁻/TiO₂¹⁻), HC₂ centres (SiO₂²⁻/TiO₂²⁻) etc. It was found that by replacing Li₂SiO₃ with an equal molar amount of Li₂TiO₃ in the Li₄SiO₄ pebbles, the total concentration of the paramagnetic RD and RP
is decreased. However, the analysis of RD and RP formation in the modified Li$_2$SiO$_4$ pebbles as a function of the Li$_2$TiO$_3$ content requires additional experiments, due to different pebble microstructures, grain sizes or contents of metallic impurities etc.

**Acknowledgments**

Research was financed by Ministry of Education and Science (Republic of Latvia), project EURATOM No. 11-11/ES12. The authors greatly acknowledge the support of L. Avotina, E. Pajuste and R. Poplausks (Institute of Chemical Physics, University of Latvia).

**References**