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# Formation and accumulation of radiation-induced defects and radiolysis products in modified lithium orthosilicate pebbles with additions of titanium dioxide

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## HIGHLIGHTS

- Formation of RD and RP in modified $Li_4SiO_4$ pebbles with additions of $TiO_2$ is analysed for the first time.
- Due to additions of $TiO_2$, concentration of paramagnetic RD slightly increased in modified $Li_4SiO_4$ pebbles.
- Modified $Li_4SiO_4$ pebbles have good radiation stability compared to reference pebbles.
- Irradiation temperature has significant impact on radiolysis of modified $Li_4SiO_4$ pebbles.

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## ABSTRACT

Lithium orthosilicate ($Li_4SiO_4$) 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 $Li_4SiO_4$ 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 $Li_4SiO_4$ pebbles and to add titanium dioxide ($TiO_2$), to obtain lithium metatitanate ($Li_2TiO_3$) as a second phase. The aim of this research was to investigate the formation and accumulation of radiation-induced defects (RD) and radiolysis products (RP) in the modified $Li_4SiO_4$ pebbles with different contents of $TiO_2$ for the first time, in order to estimate and compare radiation stability. The reference and the modified $Li_4SiO_4$ pebbles were irradiated with accelerated electrons ($E = 5$ MeV) up to 5000 MGy absorbed dose at 300–990 K in a dry argon atmosphere. By using electron spin resonance (ESR) spectroscopy it was determined that in the modified $Li_4SiO_4$ pebbles, several paramagnetic RD and RP are formed and accumulated, like, E' centres ($SiO_3^{3-}/TiO_3^{3-}$), $HC_2$ centres ($SiO_4^{3-}/TiO_3^{-}$) etc. On the basis of the obtained results, it is concluded that the modified $Li_4SiO_4$ pebbles with $TiO_2$ additions have comparable radiation stability with the reference pebbles.



## 1. Introduction

In the International Thermonuclear Experimental Reactor (ITER, Cadarache, France) several concepts of Test Blanket Modules (TBMs) will be tested and verified, because the tritium breeding is a key issue in future burning plasma machines, like, DEMO (Demonstration fusion power plant) [1–5]. The Helium Cooled Pebble Bed (HCPB) TBM, proposed by the European Union, will use lithium orthosilicate ($Li_4SiO_4$) pebbles with 2.5 wt% excess of silicon dioxide ($SiO_2$) as the reference tritium breeding ceramic [4–7]. Due to the excess of $SiO_2$, the reference pebbles have two phases – 90 mol% $Li_4SiO_4$ and 10 mol% lithium metasilicate ($Li_2SiO_3$) [8–10].

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The reference $Li_4SiO_4$ pebbles with 2.5 wt% excess of $SiO_2$ have appropriate properties for the tritium breeding, i.e. a high lithium density (up to 0.54 g $cm^{-3}$) and melting point (eutectic point at 1298 K), a good tritium release behaviour and chemical compatibility with structural materials, i.e. Eurofer steel [6,7]. However, beside the main task to produce and release tritium, the reference pebbles must also be able to withstand the harsh conditions as expected during exploitation.

The tritium breeding ceramic in the HCPB TBM will be simultaneously exposed to an intense neutron flux (up to $10^{18}$ neutrons $m^{-2}$ $s^{-1}$), ionizing radiation dose rate (up to 1 kGy $s^{-1}$), a high magnetic field (7–10 T) and elevated temperatures (570–1190 K) [1,5,11,12].

The latest neutron irradiation experiments [13] showed that the reference $Li_4SiO_4$ pebbles will likely perform sufficiently well in the HCPB TBM. However, it has also been reported that the reference pebbles may crack and form fragments during irradiation. Therefore, it has been suggested to increase the mechanical stability of the reference pebbles, so that the pebbles withstand the 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 $Li_4SiO_4$ pebbles by adding titanium dioxide ($TiO_2$) [6,7]. Due to the additions of $TiO_2$, lithium metatitanate ($Li_2TiO_3$) is obtained as a secondary phase in the modified $Li_4SiO_4$ pebbles. $Li_2TiO_3$ pebbles are also approved as a "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 [4–7,13,14]. Therefore, in combining these two phases – $Li_4SiO_4$ and $Li_2TiO_3$ – it is anticipated to obtain a modified tritium breeding ceramic with improved mechanical properties, without losing the benefit of the high lithium density, melting temperature 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 physico-chemical processes (e.g. radiolysis), phase transitions and microstructural changes, which will occur during irradiation. From previous studies [15–17], it is known that the formation, accumulation and annihilation of radiation-induced defects (RD) and radiolysis products (RP) may occur in the ceramic during irradiation. 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 [15–34].

The aim of this research was to investigate the formation and accumulation of RD and RP in the modified $Li_4SiO_4$ pebbles with different $TiO_2$ contents for the first time, in order to estimate and compare the radiation stability.

## 2. Literature review

For now, the modified $Li_4SiO_4$ pebbles with additions of $TiO_2$ have only been investigated by a few groups of researchers and thus there is a gap in the theoretical and practical knowledge about this ceramic. The first articles about the fabrication and development of the modified pebbles were published by R. Knitter et al. [7] and O. Leys et al. [35]. It was found that the additions of $TiO_2$ in the $Li_4SiO_4$ pebbles significantly increased the crush load, while the closed porosity slightly increased with increasing the content of $TiO_2$.

D. A.H. Hanaor et al. [36] made a behavioural phase transformation diagram of the quasi-binary $Li_4SiO_4$–$Li_2TiO_3$ system, to understand the phase stability and melting of the modified $Li_4SiO_4$ pebbles. It was reported that the mixed phase material shows liquid formation from the melting of the $Li_4SiO_4$ phase at temperatures >1373 K.

M. Gonzalez et al. [37] investigated the influence of the radiation-induced processes on the sorption and desorption of deuterium ($D_2$) in the modified $Li_4SiO_4$ pebbles. It was shown that the mechanisms of $D_2$ desorption in the modified pebbles highly depends on the radiation-induced effects.

However, until now, the radiolysis of the modified $Li_4SiO_4$ pebbles was not analysed, and thus additional research is required, to understand the formation, accumulation and annihilation of RD and RP during irradiation at elevated temperature. Previously, the radiolysis of the reference $Li_4SiO_4$ pebbles and the $Li_2TiO_3$ pebbles have been investigated separately.

### 2.1. Radiolysis of the reference $Li_4SiO_4$ pebbles with excess of $SiO_2$

The reference $Li_4SiO_4$ pebbles with excess of $SiO_2$ have two crystalline phases – $Li_4SiO_4$ as the primary phase and $Li_2SiO_3$ as a secondary phase. The radiolysis of the $Li_4SiO_4$ ceramic and the $Li_2SiO_3$ ceramic have been analysed and described by several authors [15–25]. Both, $Li_4SiO_4$ and $Li_2SiO_3$ have chemical bonds [≡Si–$O^-$ $Li^+$] and thus the mechanisms of the radiolysis and the structure of the formed RD and RP will be similar in both cases. Therefore, the radiolysis of a secondary phase, $Li_2SiO_3$, in the reference pebbles will not be discussed separately in this research.

The mechanism of the radiolysis is the same for the $Li_4SiO_4$ powders, pebbles, pellets and other ceramics; only the quantitative parameters of the radiolysis are different [25]. The localisation of RD and RP takes place through two stages. In the first stage, primary RD and RP localise mainly on structural defects and impurities, while in the second stage, the radiolysis of the matrix occurs. At the second stage in bulk ceramics (pebbles, pellets etc.), the formation of RD and RP proceeds slowly in comparison with the powders. Therefore, dense ceramic materials usually have higher radiation stability in comparison with powders.

A. Abramenkovs et al. [16] and J. Tiliks et al. [15,17,25] reported that the radiolysis of the reference $Li_4SiO_4$ pebbles can be divided into three main stages. In the first stage, primary electron and hole type RD, like, E' centres (≡Si• or $SiO_3^{3-}$) and $HC_2$ centres (≡Si–O• or $SiO_4^{3-}$), are formed (Eqs. (1) and (2)). The symbol "≡" represents three bonds to three oxygen atoms in the crystal structure.

$$SiO_4^{4-} \rightsquigarrow SiO_4^{3-}\ (HC_2\ centre) + e^- \tag{1}$$

$$SiO_4^{4-} + e^- \rightarrow SiO_3^{3-} (E'centre) + O^{2-} \tag{2}$$

In the second stage of the radiolysis, secondary RD, like peroxide radicals (≡Si–O–O•) and chemically stable molecular compounds – RP, are generated (Eqs. (3)–(7)). The major RP are colloidal lithium ($Li_n$), elementary silicon ($Si_n$), molecular oxygen ($O_2$), silanol (≡Si–Si≡), disilicate (≡Si–O–Si≡) and peroxide (≡Si–O–O–Si≡) bonds.

$$n\,Li^+ + n\,e^- \rightarrow Li_n \tag{3}$$

$$\equiv Si - O\cdot\ (HC_2 centre) + \ \cdot O - Si\equiv \rightarrow \equiv Si - O - Si\equiv + {}^1\!/_2\,O_2 \tag{4}$$

$$\equiv Si\cdot\ (E'centre) + O_2 \rightarrow \equiv Si - O - O\cdot \tag{5}$$

$$\equiv Si\cdot + \cdot Si\equiv \rightarrow \equiv Si - Si\equiv \tag{6}$$

$$\equiv Si - O - O\cdot + \cdot Si\equiv \rightarrow \equiv Si - O - O - Si\equiv \tag{7}$$

In the third and final stage of the radiolysis, chemical reactions between RP proceed and chemical compounds, for example lithium oxide ($Li_2O$), are formed.