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Formation and annihilation of radiation defects and radiolysis products in modified lithium orthosilicate pebbles with addition of titanium dioxide

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1. Introduction

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) [1].

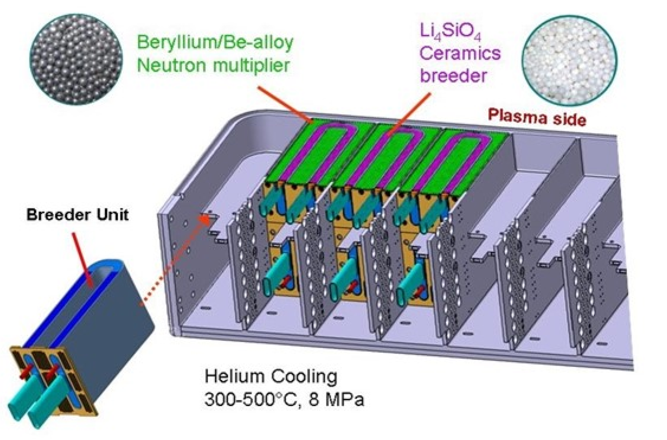


Figure 1. EU HCPB TBM [2].

PROBLEM:
The reference Li_4SiO_4 pebbles may crack and form fragments under operation conditions as expected in an HCPB TBM [3].

SOLUTION:
Replace the excess of SiO_2 by titanium dioxide (TiO_2), to obtain lithium metatitanate (Li_2TiO_3) as a second phase [4].

AIM OF WORK:
Investigate the formation and annihilation of the radiation defects and radiolysis products in the modified Li_4SiO_4 pebbles with additions of Li_2TiO_3.

2. Experimental

2.1. Investigated samples

Table 1. Specification of the investigated pebbles

Parameter	Reference pebbles	Modified pebbles		
		No. 1	No. 2	No. 3
Chemical composition	90 mol% Li_4SiO_4 10 mol% Li_2SiO_3	90 mol% Li_4SiO_4 10 mol% Li_2TiO_3	80 mol% Li_4SiO_4 20 mol% Li_2TiO_3	70 mol% Li_4SiO_4 30 mol% Li_2TiO_3
Minor impurities[1]	n.d.[2]	Pt	Pt, Ca, Al, Mg, Fe	Pt
Pebble colour	"Pearl" white	Pink-brown	Yellow	Light pink

[1] detected by XRF spectroscopy
[2] n.d. – Not detected, i.e. below detection limit

2.2. Sample irradiation and treatment

Table 2. Irradiation of the Li_4SiO_4 pebbles with accelerated electrons.

Parameter	Irradiation conditions		
	No. 1	No. 2	No. 3
Absorbed dose, GGy	1	3.5	5
Temperature, K	380-560	440-670	380-650
Average temperature, K	460	520	520
Dose rate, MGy h^{-1}	42	56	42

Table 3. Thermal treatment of the Li_4SiO_4 pebbles after irradiation with accelerated electrons.

Parameter	Conditions of thermal treatment		
Irradiation conditions	No. 1	No. 2	No. 3
Temperature, K	298-1073	-----	298-843 *(1073)*
Time, min	20	-----	20
Step, K	300	-----	30
Atmosphere	vacuum	-----	N_2

3. Main results

Properties of radiation-induced defects and radiolysis products:

3.1. Formation and accumulation

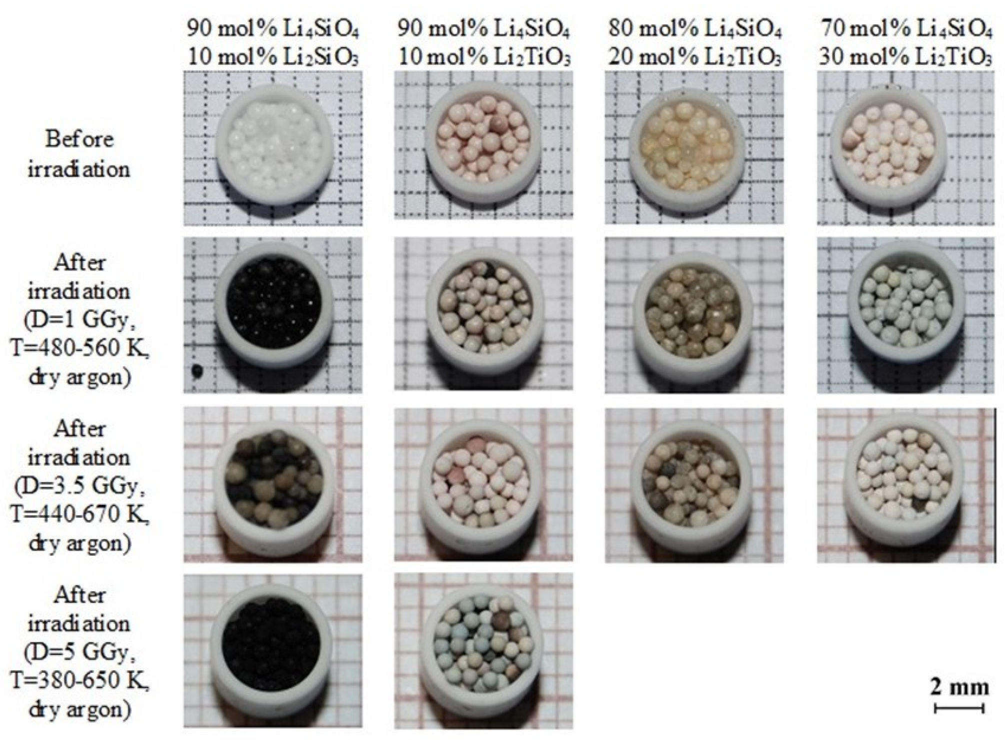
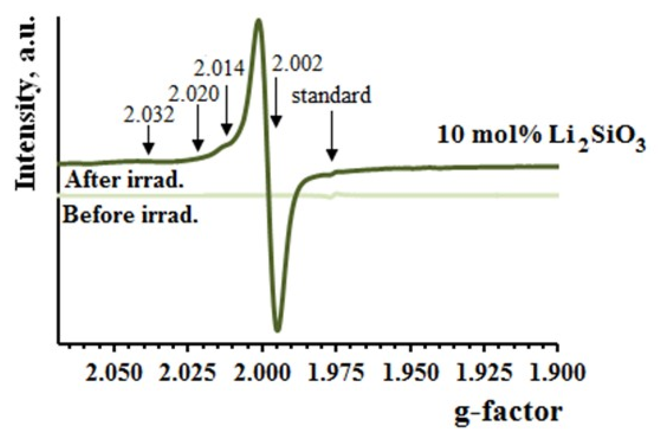


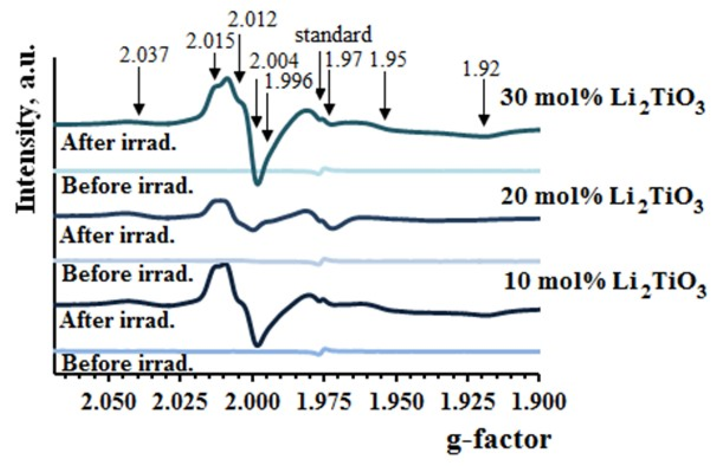
Figure 2. Photographs of the reference and modified Li_4SiO_4 pebbles before and after irradiation.

***Figures 3, 4, 7 and 8** - Electron spin resonance (ESR) spectra of the non-irradiated, irradiated and thermally treated Li_4SiO_4 pebbles*



Origin of ESR signal [5]:
2.002 – E' centre (SiO_3^{3-})
2.014 and 2.020 – HC_2 centre (SiO_4^{3-})
2.032 – peroxide radical (≡Si-O-O·)

Figure 3. The reference Li_4SiO_4 pebbles before and after irradiation (D=1 GGy, T=380-560 K).



Origin of ESR signal:
1.92, 1,95 and 1.97 - un-identified
1.996 – colloidal lithium (Li_n)
2.004 – E' centre (SiO_3^{3-}/TiO_3^{3-})
2.012 and 2.015 – HC_2 centre (SiO_4^{3-}/TiO_3^{-})
2.037 – peroxide radical (≡Si-O-O·)

Figure 4. The modified Li_4SiO_4 pebbles before and after irradiation (D=1 GGy, T=380-560 K).

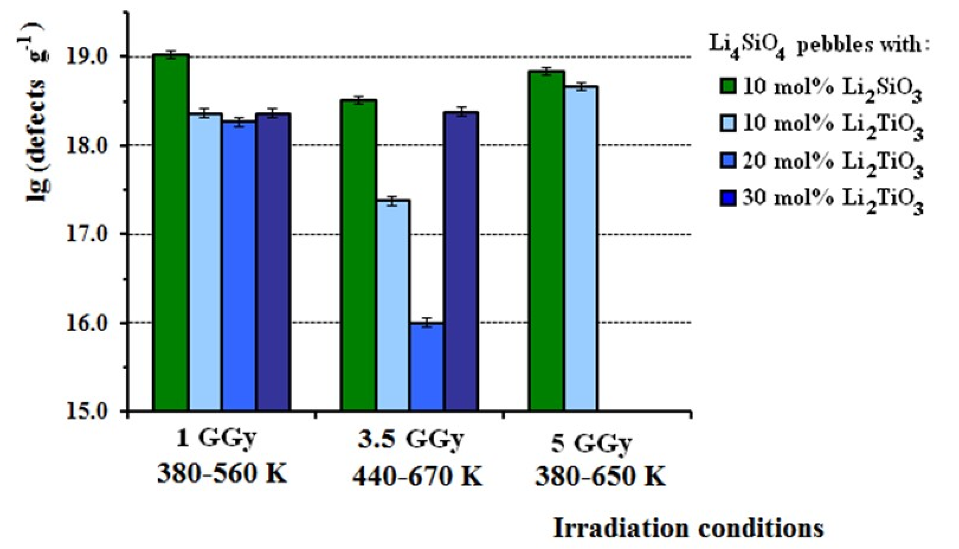


Figure 5. The total concentration of paramagnetic radiation defects and radiolysis products in the Li_4SiO_4 pebbles with different composition irradiated with accelerated electrons.

3.2. Thermal stability and annihilation

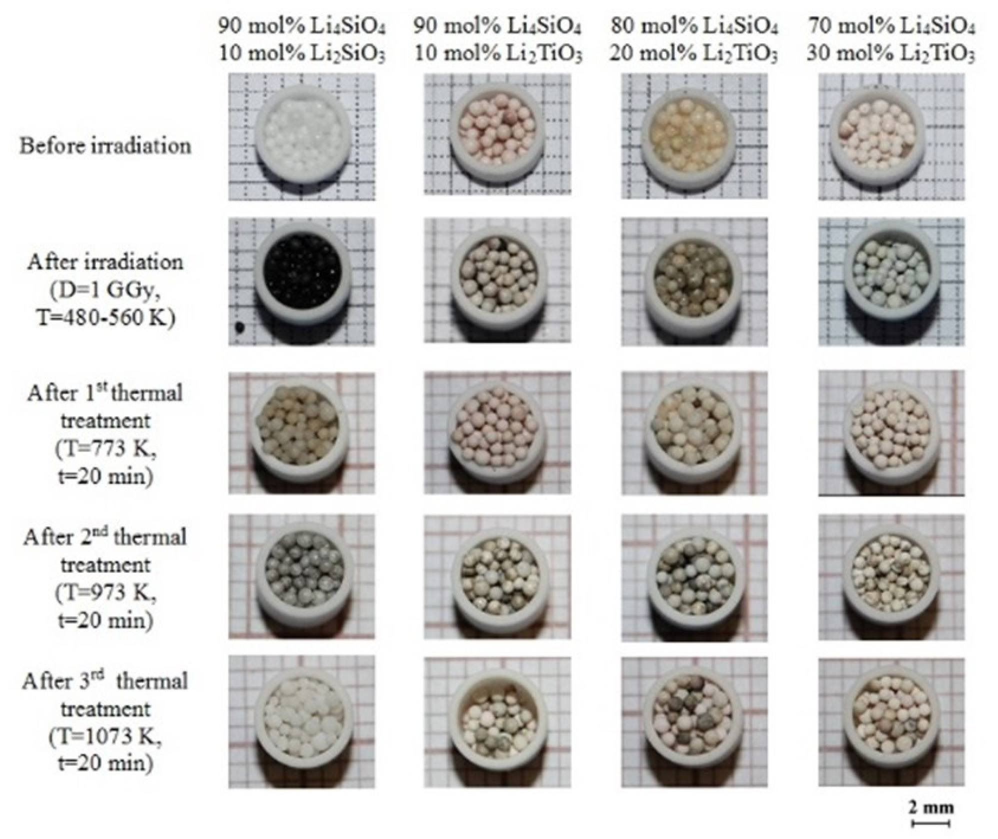


Figure 6. Photographs of the un-irradiated and irradiated Li_4SiO_4 pebbles (D=1 GGy, T=380-560 K) before and after thermal treatment in vacuum.

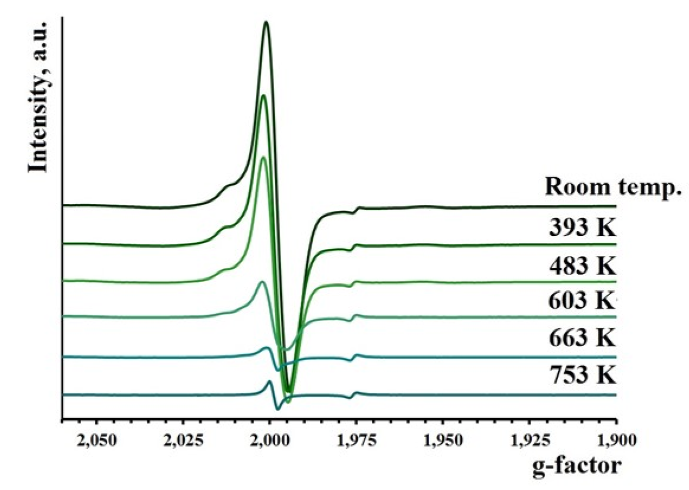


Figure 7. ESR spectra of the irradiated reference Li_4SiO_4 pebbles with 10 mol% Li_2TiO_3 (D=5 GGy, T=380-650 K) before and after thermal treatment.

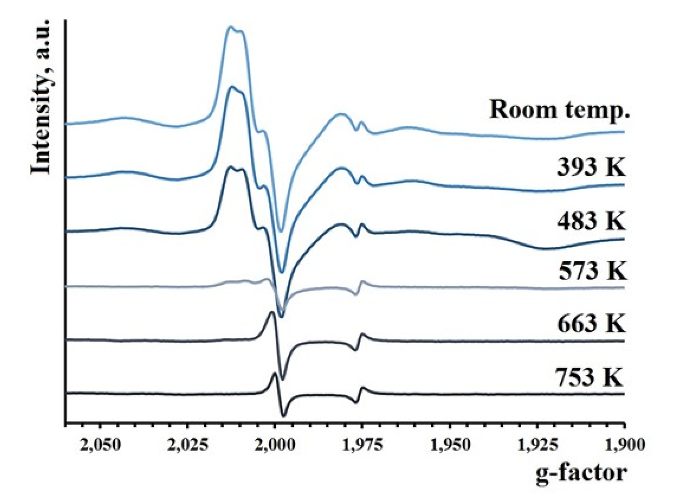


Figure 8. ESR spectra of the irradiated modified Li_4SiO_4 pebbles with 10 mol% Li_2TiO_3 (D=5 GGy, T=380-650 K) before and after thermal treatment.

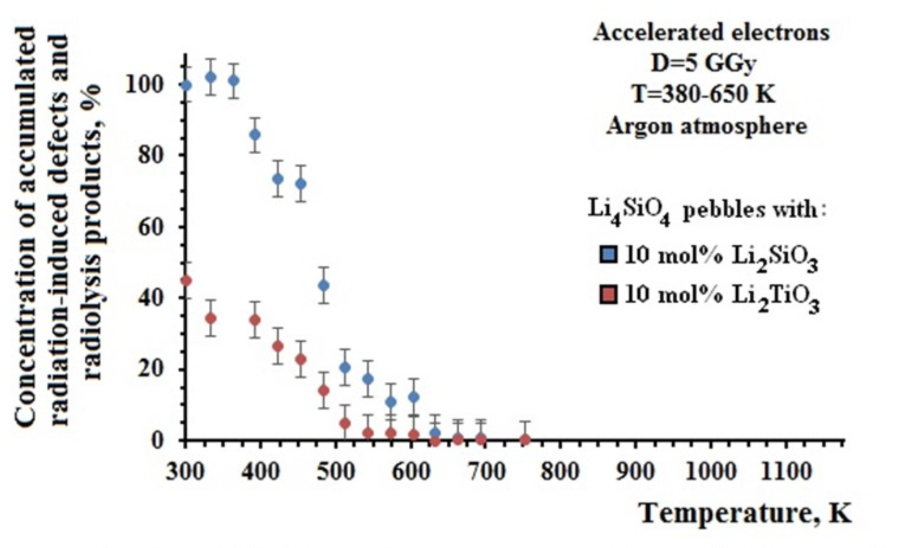


Figure 9. Annihilation of paramagnetic radiation defects and radiolysis products in the irradiated pebbles.

References

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Acknowledgments

This study was carried out in cooperation with the Faculty of Chemistry (University of Latvia). Research was financed by Ministry of Education and Science (Republic of Latvia), project EURATOM No. 11-11/ES12. The author's greatly acknowledge the financial support of University of Latvia, Academic Department.

4. Conclusions

1) **Replacing the excess of SiO_2 with equal amounts of TiO_2 decreases the total concentration of paramagnetic radiation defects and radiolysis products in the modified Li_4SiO_4 pebbles.**
2) **Up to 85-98 % of the accumulated paramagnetic radiation defects and radiolysis products in the reference and modified Li_4SiO_4 pebbles practically annihilate after thermal treatment up to 600 K.**
3) **The ESR signals of the accumulated radiation-induced defects and radiolysis products in the reference and modified Li_4SiO_4 pebbles practically disappear after thermal treatment up to 1000 K temperature.**