



Accumulation of radiation defects and products of radiolysis in lithium orthosilicate pebbles with silicon dioxide additions under action of high absorbed doses and high temperature in air and inert atmosphere

A. Zarins^a, A. Supe^a, G. Kizane^{a,*}, R. Knitter^b, L. Baumanė^a

^a Laboratory of Radiation Chemistry of Solids, Institute of Chemical Physics, University of Latvia, Kronvalda Bulvaris 4, LV-1010 Riga, Latvia

^b Karlsruhe Institute of Technology, Institute for Applied Materials (IAM-WPT), POB 3640, 76021 Karlsruhe, Germany

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ABSTRACT

One of the technological problems of a fusion reactor is the change in composition and structure of ceramic breeders (Li_4SiO_4 or Li_2TiO_3 pebbles) during long-term operation. In this study changes in the composition and microstructure of Li_4SiO_4 pebbles with 2.5 wt% silicon dioxide additions, fabricated by a melt-spraying process, were investigated after fast electron irradiation ($E = 5$ MeV, dose rate up to 88 MGy h^{-1}) with high absorbed dose from 1.3 to 10.6 GGy at high temperature (543–573 K) in air and argon atmosphere. Three types of pebbles with different diameters and grain sizes were investigated. Products of radiolysis were studied by means of FTIR and XRD. TSL and ESR spectroscopy were used to detect radiation defects. SEM was used to investigate structure of pebbles. Experiments showed that Li_4SiO_4 pebbles with a diameter of 500 μm had similar radiation stability as pebbles with diameter $<50 \mu\text{m}$ which were annealed at 1173 K for 128 h in argon and air atmosphere. As well as determined that lithium orthosilicate pebbles with size 500 (1243 K 168 h) and $<50 \mu\text{m}$ (1173 K 128 h) have a higher radiation stability in air and argon atmosphere than pebbles with size $<50 \mu\text{m}$ (1073 K 1 h). Degree of decomposition $\alpha_{10.56}$ of the lithium orthosilicate pebbles at an absorbed dose of 10.56 GGy in air atmosphere is 1.5% and 0.15% at irradiation in dry argon. It has been suggested that changes of radiation stability of lithium orthosilicate pebbles in air atmosphere comparing with irradiated pebbles in argon atmosphere is effect of chemical reaction of lithium orthosilicate surface with air containing H_2O and CO_2 in irradiation process. As well as it has been suggested that silicon dioxide – lithium metasilicate admixtures do not affect formation mechanism of radiation defect and products of radiolysis in lithium orthosilicate pebbles.

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1. Introduction

Lithium orthosilicate pebbles with 2.5 wt% silicon dioxide additions ($\text{Li}_4\text{SiO}_4 + 2.5 \text{ wt\% SiO}_2$) with diameters ranging from 250 to 630 μm fabricated by a melt-spraying process have been selected as one of possible breeder materials for the European Helium Cooled Pebble Bed (HCPB) blanket [1,2]. One of the technological problems of a fusion reactor is the change in composition and structure of ceramic breeder pebbles (Li_4SiO_4 or Li_2TiO_3) during long-term operation [3]. Our previous investigations [4] have shown that the concentration of products of radiolysis can reach a few percent during the exposure of lithium orthosilicate blankets to the ionizing radiation. Radiolysis of lithium containing ceramics may lead to changes of micro-particles' surface properties, and as a result, to deterioration of the tritium thermo-extraction parameters, mechanical and thermo-physical properties of ceramics [4].

* Corresponding author. Address: University of Latvia, Institute of Chemical Physics, Kronvalda Blvd. 4, LV-1586, Riga, Latvia. Tel./fax: +371 67033883.

E-mail address: gunta.kizane@lu.lv (G. Kizane).

Moreover, accumulation of radiation defects and products of radiolysis may cause significant changes in the mechanism of radiolysis at high doses and, accordingly, influence tritium release and retention. In addition, small concentration of impurities strongly affects the lithium orthosilicate radiolysis [4].

It must be highlighted that all previous research of radiolysis of lithium orthosilicate was done with “pure” lithium orthosilicate in the range of small absorbed doses (up to 1 GGy) and samples were irradiated at room temperature [4]. Thus the first aim of our research was to estimate the influence of silicon dioxide additions on radiation stability of lithium orthosilicate pebbles, formation of radiation defects and products of radiolysis under action of high (up to 10.6 GGy) absorbed doses of accelerated electrons, high temperatures (up to 578 K) and different atmospheres (air and argon atmosphere). These parameters of irradiation were selected according to the operating conditions of a fusion reactor, in which the blanket materials will be exploited at high temperature of 900–1100 K, under action of high magnetic field 7–10 T and intense neutron radiation of 2.4 MW m^{-2} or $10^{18} \text{ neutrons m}^{-2} \text{ s}^{-1}$ [1,2,5,6].

Table 1
Characteristics of the investigated pebbles.

No.	Pebble size (μm)	Grain size (μm)	Annealing temperature (K)	Annealing time (h)	Excess of SiO_2 , (wt%)
#1	<50	1	1073	1	2.5
#2	<50	5	1173	128	2.5
#3	500 \pm 50	10	1243	168	2.5

In the melt-spraying process pebbles with a size from 10 to 1000 μm can be produced and only 50 wt% of all pebbles were with diameter 250–630 μm [7]. At the same time approximately 40% of pebbles were with the diameter less than 250 μm . From economical point of view it would be reasonable to consider use of these pebbles as filler material to reduce space between pebbles with diameter 250–630 μm (packing factor for mono-sized particles is in the range of 63–64% [8]) in the HCPB. Thus second aim of this study was to estimate radiation stability of small pebbles (<50 μm) and compare with the stability of pebbles of 250–630 μm diameter.

To achieve both aims of research three different types of Li_4SiO_4 pebbles (Table 1) with 2.5 wt% silicon dioxide additions were synthesised with the melt-spraying process. Changes in the composition and microstructure of the Li_4SiO_4 pebbles before and after irradiation were investigated by means of electron spin resonance (ESR), thermally stimulated luminescence (TSL), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and chemical methods.

2. Experimental

Lithium orthosilicate pebbles with 2.5 wt% silicon dioxide additions ($\text{Li}_4\text{SiO}_4 + 2.5 \text{ wt}\% \text{ SiO}_2$) were fabricated by a melt-spraying process in a semi-industrial scale facility at Schott AG, Mainz, Germany [9]. For our experiments two type lithium orthosilicate pebbles with diameter <50 μm and 500 μm were selected. While larger pebbles (500 μm) crystallize during cooling, pebbles with

diameters smaller than 50 μm solidify amorphously [10]. Pebbles with a diameter of about 500 μm were annealed in order to obtain a homogeneous microstructure. Additionally, pebbles of the same fabrication campaign but with diameters of less than 50 μm were heat treated at different temperatures to achieve crystallization and a microstructure with different mean grain sizes. Characteristics of the investigated samples are summarised in Table 1.

Irradiation of pebbles was performed in quartz tubes in both air and dry argon atmosphere with accelerated 5 MeV electrons at $560 \pm 20 \text{ K}$ by means of the ELU4 accelerator (Salaspils, Latvia). The dose rate of 24.4 kGy/s was calculated from measured electron flux.

The ESR spectra of the radiation-induced free radicals where recorded by a Bruker BioSpin X-band radiospectrometer operating at 100 kHz field modulation. The XRD spectra were measured by a Bruker D5005 spectrometer (source: $\text{Cu K}\alpha$, $\lambda = 0.15418 \text{ nm}$, anode current = 40 mA, voltage = 40 kV). FTIR spectroscopy was performed by means of an AVATAR 330 FTIR Thermo Nicolet and BRUKER EQUINOX55 spectrometers. TSL was measured at a heating rate of 2 K/s. The microstructure of the pebbles was investigated at etched cross-sections by field emission scanning electron microscopy (FE-SEM, ZEISS, SUPRA 55).

3. Results and discussion

3.1. Scanning electron microscopy

The microstructure of lithium orthosilicate pebbles with silicon dioxide additions after annealing at etched cross-sections is shown in Fig. 1. The different grain sizes of the samples before irradiation can be seen in the upper row. In samples #2 and #3 lithium orthosilicate is displayed in dark-grey with smaller, light-grey grains of lithium metasilicate as inter- or intra-crystalline inclusions. Because of the small grain size, lithium metasilicate cannot be detected in sample #1. In sample #2 the grains seem to be only loosely connected, and some of the pebbles were already destroyed during

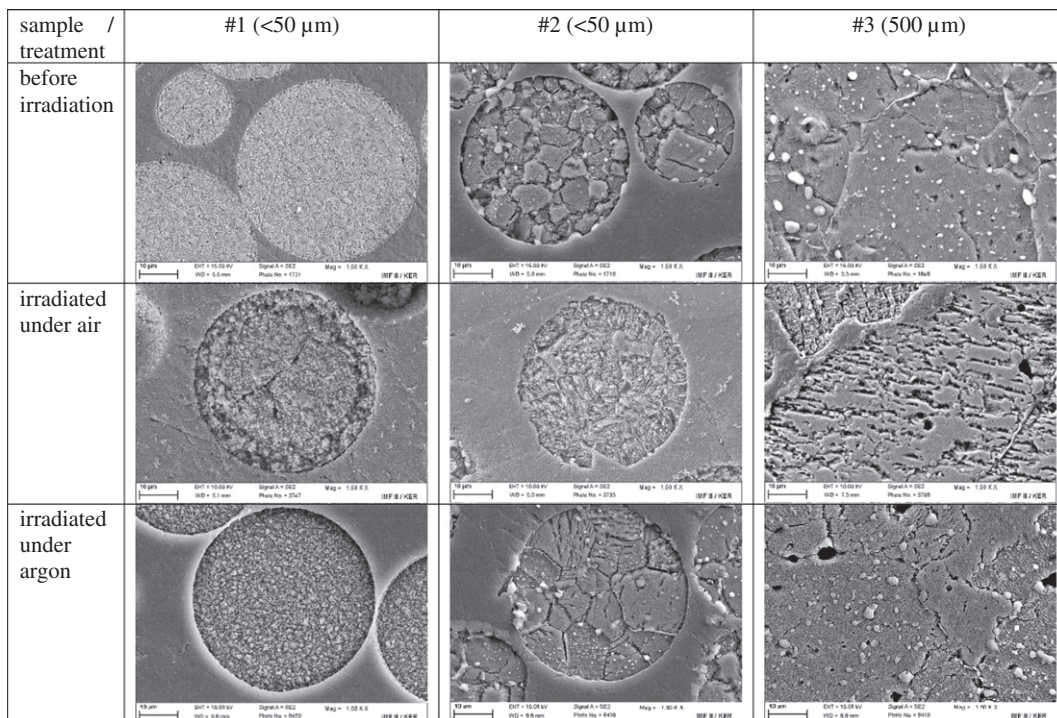


Fig. 1. Microstructure of pebbles at etched cross-sections before and after irradiation with an absorbed dose of 10.56 GGy.

grinding and polishing. This may be caused by an improper heat treatment during crystallization of the previously amorphous pebbles. After irradiation in air, all samples exhibit a fissured microstructure, and the smaller pebbles (samples #1 and #2) nearly appear to be disintegrated (middle row of Fig. 1). Different phases are hardly distinguishable by SEM. But after irradiation in argon, the samples are nearly unchanged (lower row in Fig. 1). The small pebbles seem to exhibit a slightly more porous microstructure with more gaping grain boundaries, but there is hardly any difference in the microstructure of the large pebbles compared to the unirradiated material. The second phase, lithium metasilicate, can also be detected as inter- or intra-crystalline inclusions in samples #2 and #3. As lithium orthosilicate is easily etched with a mixture of water and ethanol in only a few seconds, the preparation of cross-sections is subject to fluctuations. Especially lithium orthosilicate with small grain sizes is rapidly etched too much, so that the appearance of cross-sections may display a corrosion effect and therefore has to be regarded with suspicion. Nevertheless, the samples irradiated under air atmosphere appear to be chemically eroded by possible reactions with air, containing H₂O and CO₂.

3.2. Electron spin resonance spectroscopy

ESR spectra of all investigated samples of pebbles after irradiation with doses up to 10.56 GGy exhibit at least three different lines with *g*-factors of 2.001, 2.011 and 2.016. Those spectra are similar to the ones previously reported for irradiated “pure” Li₄SiO₄ [11] and can be interpreted as superposition of signals from so-called E' and HC₂ centres (ion radicals SiO₃³⁻ and SiO₄³⁻, respectively). Ion radical SiO₃³⁻ (HC₂ centre) in ESR spectra is presented with 2 lines (*g*_± = 2.009 and *g*_{||} = 2.016) due to anisotropy of the *g*-factor. A very

weak and broad multiplex signal was also observed at ESR spectra of irradiated sample #1. This signal can be attributed to electrons localised in anion or oxygen vacancy (so called F⁺ centres). ESR spectra of all three samples irradiated in air atmosphere with a dose of 10.56 GGy contain two symmetric lines with 50.2 mT splitting, typical for localised hydrogen atoms. Beside this, several unidentified lines possibly due to impurities were observed at ESR spectra of samples irradiated with a dose of 10.56 GGy in air atmosphere. Concentrations of stabilised paramagnetic centres in pebbles irradiated with doses from 1 to 5 GGy are in the range of 10¹⁵–10¹⁶ radicals g⁻¹ and slightly increase with increasing absorbed dose. Concentration of free radicals stabilised in samples irradiated in dry argon with absorbed doses of less than 2 GGy are significantly higher than in case of samples irradiated in air atmosphere. For samples irradiated in dry argon an increase of the absorbed dose higher than 5 GGy cause a decrease of radicals' concentration. On the other hand, a surprisingly high concentration of stabilised paramagnetic centres (10¹⁷–10¹⁹ radicals g⁻¹) was observed in samples irradiated with a dose of 10.56 GGy in air atmosphere (see Table 2). Thus, in irradiated pebbles the same radiation defects are stabilized that were previously detected in “pure” Li₄SiO₄, but the concentration of stabilized free radicals at doses from 1 to 5 GGy is approximately 2 times higher (ESR measurements of “pure” Li₄SiO₄ irradiated with a dose of 10.56 GGy were not made previously) [11].

3.3. Thermally stimulated luminescence

TSL curves of irradiated lithium orthosilicate pebbles are also similar to the ones previously reported for irradiated “pure” Li₄SiO₄ [11] and contain three maxima at temperatures of 395 ± 25, 438 ± 12 and 500 ± 50 K. In the high temperature region the fourth

Table 2
Characteristics of ESR spectra.

Sample	Atmosphere, dose (GGy)	Radical	<i>g</i> -Factor	Splitting (mT)	Concentration, 10 ¹⁶ radicals g ⁻¹
#1	Air, 1.32	E'	2.0013	None	0.002
		HC2	2.0154; 2.0093	None	0.080
		F ⁺	2.0022	Unresolved	0.009
#1	Air, 2.64	E'	2.0026	None	0.03
		HC2	2.0157; 2.0108	None	0.07
#1	Air, 5.28	E'	2.0013	None	0.09
		HC2	2.0156; 2.0095	None	0.07
#1	Argon, 5.28	E'	2.00	None	0.9
		HC2	2.015; 2.008	None	9.4
#1	Air, 10.56	E'	2.0011	None	2250
		HC2	2.0154; 2.0069	None	5
		H	2.0023	50.2	1
#1	Argon, 10.56	E'	2.0012	None	25.1
		HC2	2.015; 2.0075	None	1.4
		F ⁺	2.0022	Unresolved	1
#2	Air, 1.32	E'	2.0018	None	0.02
		F ⁺	2.0022	Unresolved	0.01
		E'	2.00	None	0.5
#2	Air, 2.64	E'	2.001	None	2.5
		E'	2.001	None	2.5
#2	Air, 5.28	HC2	2.015; 2.0065	None	0.1
		E'	2.0015	None	6.5
#2	Air, 10.56	HC2	2.015; 2.0085	None	0.4
		H	2.002	50.2	0.1
		E'	2.001	None	0.04
#2	Argon, 10.56	HC2	2.015; 2.0075	None	0.04
		E'	2.001	None	0.09
#3	Air, 1.32	HC2	2.015; 2.005	None	0.01
		E'	2.001	None	0.03
#3	Air, 2.64	E'	2.001	None	0.39
		HC2	2.015; 2.005	none	0.02
#3	Air, 5.28	E'	2.001	None	0.3
		HC2	2.015; 2.008	None	0.05
#3	Argon, 5.28	E'	2.0013	None	39
		HC2	2.0138; 2.0079	None	12
		H	2.002	50.2	1
#3	Air, 10.56	E'	2.001	None	0.4
		E'	2.001	None	0.4

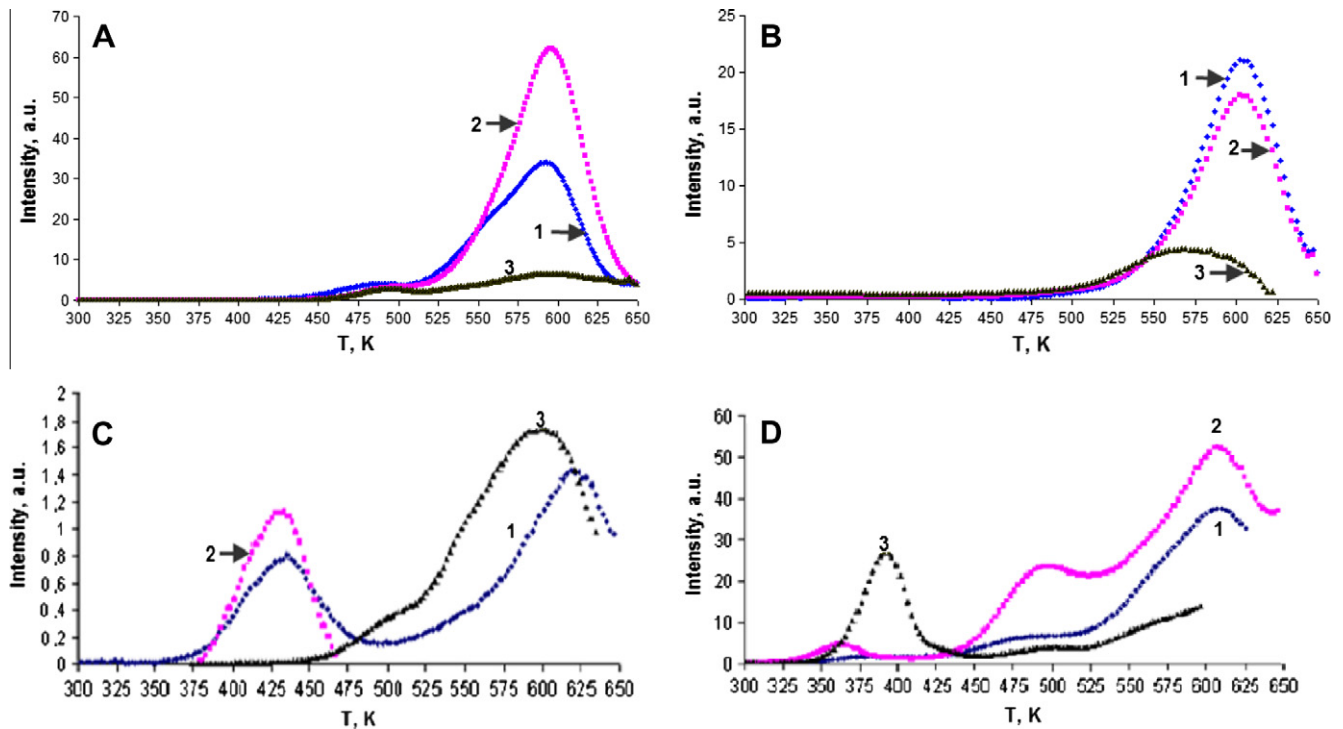


Fig. 2. TSL curves of lithium orthosilicate pebbles after irradiation with doses of 2.64 (A and C) and 10.56 (B and D) GGy in dry argon (A and B) and air (C and D) atmosphere (numbering of curves corresponds to numbers of investigated samples given in Table 1). Curve 3C is decreased 30 times, curve 2D is decreased 3 times.

maximum is observed at 612 ± 38 K (see Fig. 2). The maximum at 500 ± 50 K is unstable and disappears within 60 days after irradiation. The TSL intensity of samples irradiated in dry argon is significantly higher than that for samples irradiated in air atmosphere. In TSL curves of pebbles irradiated in argon the intensities of the maximum in the high temperature region (612 ± 38 K) are higher by factor 10–100 than intensities of other maxima. This may be due to the high temperature (up to 587 K) of irradiation. Beside this, in case of samples irradiated in argon the intensities of the first three maxima (395, 438 and 500 K) strongly decrease with the increasing of absorbed dose, but at the high irradiation doses ($D > 5$ GGy) only the fourth maximum (at 612 K) can be observed. On the other hand in TSL curves of samples irradiated in air atmosphere relatively high intensities of low-temperature peaks (at 400, 440 and 500 K) were observed at dose 10.56 GGy. It might be assumed that this effect is caused by high concentration of impurities (Li_2O , LiOH , Li_2CO_3 and other products of radiolysis) in irradiated samples. An explanation of this phenomenon can only be made after further investigation of post-irradiation processes in irradiated lithium orthosilicate pebbles with silicon dioxide additions. TSL optical spectra of all investigated samples indicate a maximum at 3.5 eV. Only TSL optical spectra of pebbles irradiated with a dose less than 1 GGy have a maximum at 2.9 eV. Both these maxima have previously been observed in TSL and radioluminescence spectra of “pure” Li_4SiO_4 [11]. The luminescence band with the maximum at 3.5 eV is due to excited states of SiO_4^{4-} anions (so called “L-centres”, [4]). The origin of the luminescence band with a maximum at 2.9 eV is not yet clear, but it is assumed that it is due to excited states of electrons localised in structure defects (so called “F⁺-centres”). Light absorption spectra registered by means of light diffuse refraction spectroscopy have a maximum at 3.0 eV (415 nm).

3.4. X-ray diffraction and Fourier transform infrared spectroscopy

Fig. 3 exemplarily displays the XRD spectra of sample #1 and #3 before and after irradiation at 10.56 GGy. While for sample #3 no

change in the phase composition, not even after the irradiation in air could be detected by XRD, the diffraction diagram of sample #1 after irradiation in air exhibits significant amounts of impurities. Due to the large amount of phases, only LiOH , $\text{LiOH}\cdot\text{H}_2\text{O}$ and traces of Li_2CO_3 could be verified, however, traces of lithium oxide cannot be ruled out. In samples #1 and #2 irradiated in air atmosphere, a significant increase of the initial concentration of Li_2SiO_3 as well as characteristic lines for LiOH and Li_2CO_3 were detected with both mentioned methods. As the specific surface area of samples #1 and #2 is 1000 times higher than of sample #3, surface reactions with H_2O and CO_2 are significantly increased in samples with a smaller pebble size. Unfortunately it was not possible to determine the concentration of products of radiolysis by means of XRD or FTIR spectroscopy. According to FTIR spectroscopy, in all three samples irradiated in air with a dose of 10.56 GGy the concentration of Li_2SiO_3 formed during irradiation is approximately 1 wt% or 4.5 mol%. On the other hand, the concentration of metasilicate in samples irradiated in argon is practically unchanged. Therefore the degree of radiolysis for samples irradiated in argon atmosphere was determined by means of chemical method, described earlier [4,12]. The obtained concentrations of colloidal lithium and other reducing products of radiolysis and radiation defects were equal to 4.4×10^{19} , 1.2×10^{19} , and 3.1×10^{19} radicals g^{-1} for samples Nos. #1, #2 and #3, respectively. As can be seen from Fig. 1, the microstructure of pebbles irradiated in argon is virtually identical to the microstructure of the corresponding unirradiated sample (except sample #1, where small changes can be observed).

3.5. Discussion

Three different types of Li_4SiO_4 pebbles with 2.5 wt% silicon dioxide additions were investigated – two samples of small pebbles with diameter $< 50 \mu\text{m}$ (annealed at 1073 K for 1 h and 1173 K for 128 h) and standard pebbles with diameter $500 \pm 10 \mu\text{m}$ (annealed at 1243 K for 168 h), which were synthesised with melt-spraying process and annealed at different

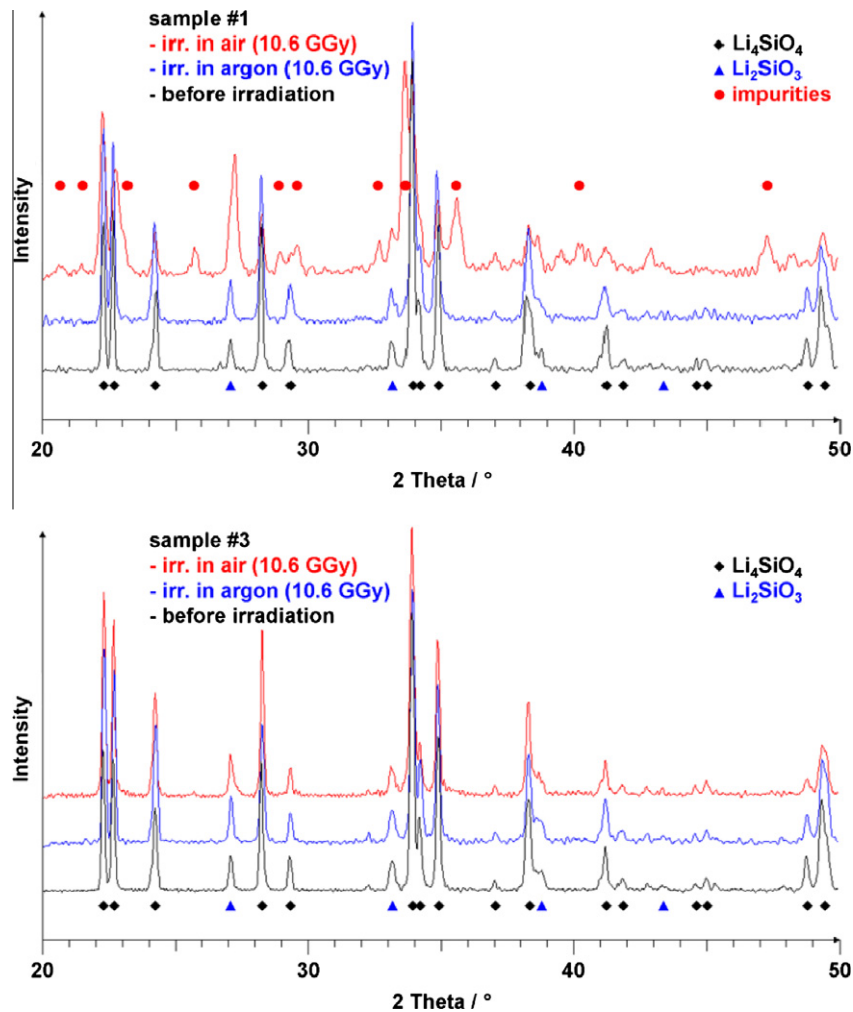
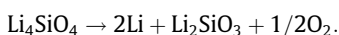


Fig. 3. XRD spectra of sample #1 (top) and sample #3 (below) before and after irradiation with an absorbed dose of 10.56 GGy.

temperature and different time in order to understand radiation stability. All three types of pebbles have a main crystalline phase, lithium orthosilicate (~90%), and a second minor phase, lithium metasilicate (~10%). In the same time only pebbles with a diameter <50 μm (annealed at 1073 K for 1 h) and $500 \pm 10 \mu\text{m}$ (annealed at 1243 K for 168 h) have a homogeneous structure. In pebbles with diameter <50 μm (annealed at 1173 K for 128 h) the grains are only loosely connected.

Under action of accelerated electrons (5 MeV) high absorbed dose (10.56 GGy) and high temperature (560 K) in inert atmosphere structure of all three types of lithium orthosilicate pebbles is nearly unchanged. In both small pebbles (<50 μm) hardly any difference in the microstructure is visible compared to the large ($500 \pm 10 \mu\text{m}$) pebbles. In irradiated Li_4SiO_4 pebbles in inert atmosphere new phases which can be detected with XRD do not form, but at the same time radiation defects form in lithium orthosilicate pebbles – ion radicals SiO_3^{3-} and SiO_4^{3-} and trapped electron in oxygen vacancy and products of radiolysis – colloidal lithium and Li_2SiO_3 . Thus it can be concluded that silicon dioxide additions – lithium metasilicate, do not affect formation mechanism of radiation defect and products of radiolysis in lithium orthosilicate pebbles. Similar to the results reported for the chemical methods, FT-IR and XRD for irradiated Li_4SiO_4 pebbles with 2.5 wt% SiO_2 additions are in a good agreement with the assumption that radiolysis of Li_4SiO_4 can be described by the following summary equation:



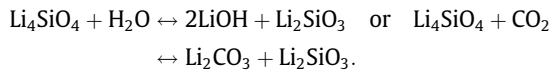
Total concentration of ion radicals in small lithium orthosilicate pebbles (<50 μm , 1073 K for 1 h) is 27.5×10^{16} radicals g^{-1} , but in larger pebbles (500 μm , 1243 K for 168 h) only 0.4×10^{16} radicals g^{-1} . Thus it can be concluded that pebbles with diameter <50 μm which are annealed at 1073 K for 1 h are radiation unstable comparing with pebbles with diameter 500 μm in air atmosphere.

In same time it should be highlighted that under action of accelerated electrons in small pebbles (<50 μm) which are annealed at 1173 K for 128 h total concentration of radiation defects reduces to 0.08×10^{16} radicals g^{-1} . Thus concentration of ion radicals is much more less than in pebbles with diameter 500 μm .

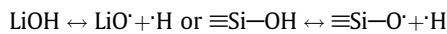
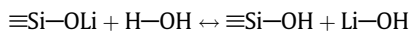
Thus it can be concluded that pebbles with diameter <50 (1173 K 128 h) and 500 μm (1243 K 168 h) have similar radiation stability in argon atmosphere, but pebbles with diameter <50 μm (1073 K 1 h) – has less stability. These results of small pebbles (<50 μm , 1073 K 1 h) can be explained by structural defects which form at melting-spray synthesis, but thermal treating of these pebbles at 1173 K temperature for 128 h reduces concentration of structural defects and increases radiation stability of pebbles.

Both high absorbed dose (10.56 GGy) and high temperature (560 K) changes radiolysis of lithium orthosilicate pebbles with SiO_2 admixes under action of air atmosphere – in all three types of pebbles more or less structure has been changed after irradiation. As well as comparing in air atmosphere irradiated pebbles with argon atmosphere irradiated pebbles observes higher concentration of radiation defects and products of radiolysis. Total

concentration of ion radicals 0.4×10^{16} radicals g^{-1} is much more less, for the largest pebbles ($500 \pm 10 \mu m$) irradiated in argon atmosphere as for pebbles irradiated in air atmosphere. In this case total concentration of ion radicals increases substantially up to 52×10^{16} radicals g^{-1} . Fast change of radiation stability of lithium orthosilicate pebbles can be explained by chemical reaction of lithium orthosilicate with air containing substances – H_2O and CO_2 in irradiation process [13–15]:



This suggestion confirms the results of the spectra of FT-IR and XRD of irradiated pebbles in air atmosphere. Traces of $LiOH$, Li_2CO_3 and lithium metasilicate can be observed. Similarly, the formation of water chemisorption products in lithium orthosilicate pebbles with silicon dioxide additions indicates atomic hydrogen which can be observed in ESR spectra of pebbles, irradiated in air atmosphere [13]:



Water and carbon dioxide chemisorption products – lithium hydroxide and lithium carbonate are radiation unstable compounds and admixing of these compounds can affect radiation stability changes of lithium orthosilicate pebbles in air atmosphere under action of high absorbed doses and high temperature.

Formation of $LiOH$ and Li_2CO_3 may significantly be increased by surface reactions, especially for pebbles with small diameters and large surface areas [15]. Specific surface of small pebbles ($<50 \mu m$) is ~ 100 times higher than for pebbles with “normal” diameter ($500 \mu m$). By that in small pebbles ($<50 \mu m$) under irradiation in air atmosphere changes of structure and composition are greater than in pebbles with “normal” diameter ($500 \mu m$).

For example the total concentration of ion radicals in small pebbles ($<50 \mu m$) annealed 1073 K for 1 h is 22.56×10^{18} radicals g^{-1} , but for large pebbles with diameter $500 \mu m$ (annealed 1243 K for 168 h) is only 0.52×10^{18} radicals g^{-1} . At same time the total concentration of radiation defects in small pebbles which are annealed at 1173 K for 128 h is considerably smaller – 0.07×10^{18} radicals g^{-1} . Thus it can be concluded that pebbles with diameter $<50 \mu m$ (1073 K 1 h) in air atmosphere are radiation unstable but pebbles with diameter <50 (1173 K 128 h) and $500 \mu m$ (1243 K 168 h) in air atmosphere are more radiation stable.

It highlighted that the degree of decomposition $\alpha_{10.56}$ of the lithium orthosilicate matrix at an absorbed dose of 10.56 GGy calculated from estimated concentration of radiolytic lithium metasilicate is approximately equal to 1.5% for irradiation in air atmosphere and 0.15% for irradiation in dry argon. This is significantly lower than the value $\alpha_{10.56} \approx 5\%$ calculated on base of empiric equation [4]:

$$\alpha_D(\%) \approx 5 \times 10^{-2} \cdot D^{0.5}$$

where D is absorbed dose, MGy.

Comparison of the obtained data of investigated pebbles allow to conclude that the lithium orthosilicate pebbles ($Li_4SiO_4 + 2.5 \text{ wt\% } SiO_2$) with size $500 \mu m$ (1243 K 168 h) and

$<50 \mu m$ (1173 K 128 h) have a higher radiation stability in air and argon atmosphere than pebbles with size $<50 \mu m$ (1073 K 1 h), but comparison of the obtained data for pebbles with a diameter of $500 \mu m$, which represent the potential material for the European test blanket module, have similar radiation stability with pebbles with diameter $<50 \mu m$ which are annealed at 1173 K for 128 h in argon and air atmosphere.

4. Conclusions

Lithium orthosilicate pebbles ($Li_4SiO_4 + 2.5 \text{ wt\% } SiO_2$) with size $500 \mu m$ (1243 K 168 h) and $<50 \mu m$ (1173 K 128 h) have a higher radiation stability in air and argon atmosphere than pebbles with size $<50 \mu m$ (1073 K 1 h). Li_4SiO_4 pebbles with a diameter of $500 \mu m$ have similar radiation stability with pebbles with diameter $<50 \mu m$ which are annealed at 1173 K for 128 h in argon and air atmosphere. Radiation stability of Li_4SiO_4 pebbles depend on both diameter that is connected with grain size and thermal treatment temperature. The degree of decomposition $\alpha_{10.56}$ of the lithium orthosilicate pebbles with silicon dioxide addition at an absorbed dose of 10.56 GGy in air atmosphere is 1.5% and 0.15% for irradiation in dry argon. It has been suggested that changes of radiation stability of lithium orthosilicate pebbles in air atmosphere comparing with irradiated pebbles in argon atmosphere is effect of chemical reaction of lithium orthosilicate surface with air containing substances – H_2O and CO_2 in irradiation process. It has been suggested that silicon dioxide – lithium metasilicate admixtures do not affect the formation mechanism of radiation defect and products of radiolysis in lithium orthosilicate pebbles.

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