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Radiation damage and tritium release from Li–Zr–Si oxides

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Abstract

Li–Zr–Si mixed oxides were irradiated in a mixed radiation field in order to produce tritium through the $Li^6(n,\alpha)H^3$ reaction. The Li–$ZrSiO_4$ samples, prepared with different Li : Zr molar ratios (1, 3, 5 and 6), presented high tritium diffusion compared with other lithium ceramics like Li_2SiO_3 and Li_2ZrO_3. Furthermore, their composition and structure were not modified after irradiation. It was also found that $Li_2ZrSi_6O_{15}$ was damaged by irradiation, and that tritium release was moderate in this compound.

Keywords: Breeder materials; Lithium ceramics; Radiation damage; Tritium and zircon

1. Introduction

Lithium ceramics have been found, since the 1980's, to be promising breeder materials for fusion reactors since they produce tritium through the $Li^6(n,\alpha)H^3$ reaction. The produced tritium is, then, diffused and released from lithium ceramics through a complex process determined, among other factors, by grain size, grain boundary and surface reactions [1,2]. Tritium diffusion and tritium release from lithium ceramics is conditioned not only by the composition of the lithium ceramic but also by the structure and texture. Furthermore, tritium is usually released with a sweep gas, helium or argon, enriched with hydrogen to enhance the process [3,4], this is another parameter which may explain the differences in the reported rates of diffusion which vary, indeed, over six orders of magnitude [5].

Still, the ideal breeder material must release as much tritium as possible and it has to be stable under extreme mechanical, thermal or chemical conditions [6–8]. The ceramics that seem to fulfill some of these requirements are lithium aluminates, lithium silicates and lithium zirconates [9–13]. Although lithium metasilicate (Li_2SiO_3) presents a good tritium diffusion and release behaviour [10,11, 14], it is not stable at temperatures higher than 1073 K [11]. On the other hand, lithium metazirconate (Li_2ZrO_3) presents a much better thermal stability (up to 1673 K), but the corresponding tritium release is only moderate in comparison to that of lithium metasilicate [11].

Its seems, therefore, that a lithium silicozirconate would be an appropriate compromise. We have focused our attention on $Li_2ZrSi_6O_{15}$, which has previously been synthesized [15–17] and Li–$ZrSiO_4$ compounds, which may be obtained from zircon ($ZrSiO_4$), which is chemically and thermally stable at temperatures as high as 2773 K [18–20]. In our research we have tested these compounds and studied the tritium release and their radiation resistance. Results on Li_2SiO_3 and Li_2ZrO_3 are also reported for comparison purposes.

2. Experimental procedures

Li–$ZrSiO_4$ and $Li_2ZrSi_6O_{15}$ samples were prepared by the sol–gel method. The details of their preparation, characteristics and properties have been previously published [17, 21]. The lithium silicozirconate sample, also alluded in this text as $Li_2ZrSi_6O_{15}$, contained 89% of $Li_2ZrSi_6O_{15}$, 5% of SiO_2 and 6% of ZrO_2 [17]. Li–$ZrSiO_4$ was synthesized at various Li : Zr molar ratios (1, 3, 5 and 6) [21]. For comparison purposes Li_2SiO_3 and Li_2ZrO_3 were also prepared as reported previously [9].

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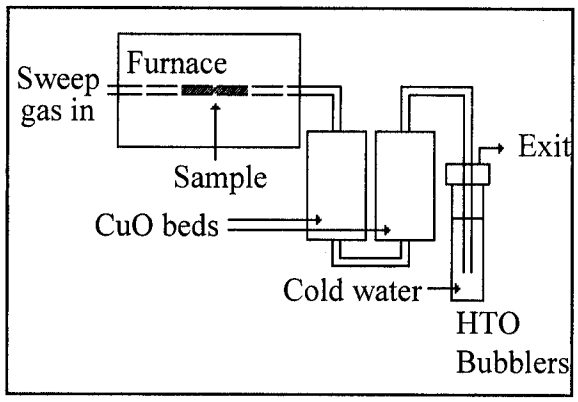

Fig. 1. Scheme of the thermal annealing device for tritium analysis.

100 mg of each sample sealed in a vial were encapsulated with two other vials, each containing 120 mg of dehydrated oxalic acid ($C_2O_4H_2$) as secondary dosimeters [22]. The capsules were irradiated for 1 h in a TRIGA Mark III nuclear reactor.

All samples were characterized before and after irradiation by X-ray diffraction (XRD). A diffractometer (D500 Siemens) coupled to a copper anode tube was used. The $K\alpha$ wavelength was selected with a diffracted beam monochomator. A Gemini 2360 Surface Area Analyzer Micromeritics equipment was used to determine the surface area of the samples. The morphology of the solids was studied by scanning electron microscopy (SEM, Philips XL-30), the samples were covered with gold to avoid the lack of electrical conductivity.

The samples were irradiated with thermal neutrons in the TRIGA Mark III nuclear reactor at the Centro Nuclear de México, up to 9×10^{12} $n_t\,cm^{-2}$ at room temperature. Furthermore, solid oxalic acid was used as a secondary standard dosimeter to measure the absorbed doses [22].

Fig. 1 shows the scheme of the tritium recovery device. It was built according to previous papers [23–25]. The irradiated samples were annealed in a stainless steel tube and then heated in a furnace at 600 K. The sweep gas employed was $Ar + 0.5\,vol\%\,H_2$ flowing at a rate of 200 $ml\,min^{-1}$. The tritium recovery was carried out as HT and/or HTO through two copper oxide (CuO, Aldrich) beds, which were heated up to 600 K, to ensure the oxidation of HT to HTO. Then HTO was trapped in cold water (200 ml). Aliquots (1 ml) were taken at different intervals for several hours. Each aliquot was placed in a scintillation vial along with 19 ml of scintillation cocktail (Ultima Gold AB, Packard). The scintillation equipment employed for the measurements was a TRI-CARB 2700TR Liquid Scintillation Analyzer, Packard. However, the tritium recovered in the water had to be compared with the total tritium present in the sample. In order to determine the total tritium in the solid samples were dissolved in a mixture of HF and HCl (0.5 N–6 N) [5]. Then, the acid solution was diluted and 1 ml aliquot was removed and placed in a scintillation vial with 19 ml of scintillation cocktail. Finally, the samples were measured as before to determine the total tritium concentration in the solid samples.

Table 1
Results obtained with oxalic acid dosimeters

Sample	Absorbed dose (MGy)
$Li_2ZrSi_6O_{15}$	1.202
Li–$ZrSiO_4$, (Li:Zr = 1)	1.390
Li–$ZrSiO_4$, (Li:Zr = 3)	1.165
Li–$ZrSiO_4$, (Li:Zr = 5)	1.390
Li–$ZrSiO_4$, (Li:Zr = 6)	1.247

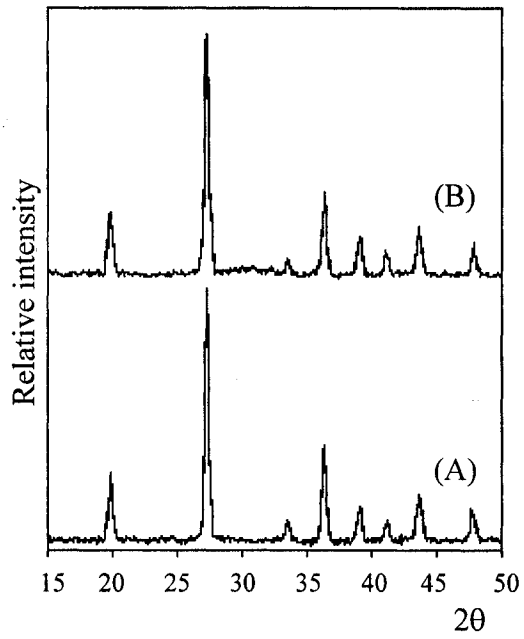

Fig. 2. XRD patterns of Li–$ZrSiO_4$ with Li:Zr molar ratio of 1 : 1, (A) before and (B) after irradiation.

3. Results and discussion

3.1. Characterization

Li–$ZrSiO_4$ samples were not visually modified by the mixed radiation field of the nuclear reactor, and the powders were white opaque before and after the irradiation. Instead, the $Li_2ZrSi_6O_{15}$ powder changed from white opaque to yellowish opaque as a consequence of the irradiation. All samples received similar irradiation doses, around 1 MGy, no corrections for different absorbed doses were necessary, Table 1.

The XRD patterns showed that the crystalline composition of Li–$ZrSiO_4$ samples did not vary with the irradiation. Fig. 2 compares the diffractograms of Li–$ZrSiO_4$ (Li:Zr molar ratio of 1) before and after the irradiation. Instead, in $Li_2ZrSi_6O_{15}$ diffractograms, ZrO_2 and SiO_2 percentages increased as a consequence of the irradiation from 6 to 11% and from 5 to 12%, respectively. Hence, the $Li_2ZrSi_6O_{15}$ amount decreased from 89 to 77% (Fig. 3). Lithium silicates

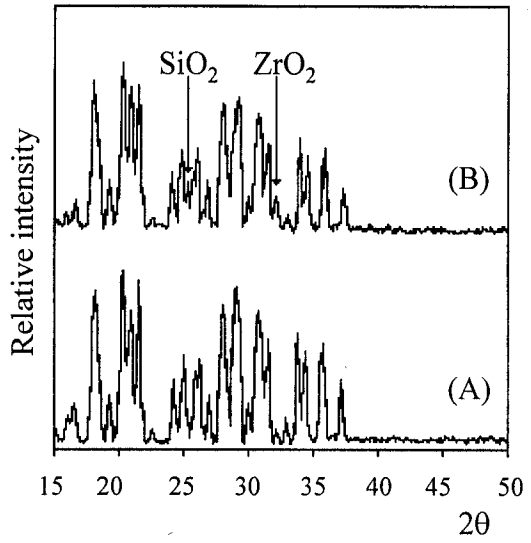

Fig. 3. XRD patterns of $Li_2ZrSi_6O_{15}$, (A) before and (B) after irradiation.

Table 2
Surface area by BET method of the samples

Sample	Area ($m^2\ g^{-1}$)	
	Before irradiation	After irradiation
$Li_2ZrSi_6O_{15}$	9.2	3.1
Li–$ZrSiO_4$, (Li : Zr = 1)	15.0	14.8
Li–$ZrSiO_4$, (Li : Zr = 3)	14.7	14.1
Li–$ZrSiO_4$, (Li : Zr = 5)	15.8	15.0
Li–$ZrSiO_4$, (Li : Zr = 6)	14.9	15.2

and $Li_2ZrSi_6O_{15}$ have chemical bonds of the form ≡Si–O–Li. The changes observed in the composition of the irradiated $Li_2ZrSi_6O_{15}$ may be attributed to the radiolysis reaction between the sample and the mixed radiation field of the nuclear reaction [27,29]. After irradiation, radiation defects and/or radiolysis products can produce ≡Si–O^0, ≡Si^0, Li^0, Li^+, vacancies, F centres, ≡Si–O–O–Si≡ and/or ≡Si–O–Si≡ among other radicals and bonds. Finally, these radicals and bonds may react to form Li_2O, SiO_2, SiO and Li_2O_2 among others [29]. Therefore, irradiation on $Li_2ZrSi_6O_{15}$ produced, as expected, SiO_2 and ZrO_2, however, vacancies, defects and some radicals were already present as not all radicals and bonds could have reacted between them to form SiO_2 and ZrO_2. Actually, the color change after powder irradiation may be attributed to the presence of vacancies and defects. The structure of $Li_2ZrSi_6O_{15}$ favour the radiolysis reactions and explains that this compound is definitely less stable than Li–$ZrSiO_4$ samples.

Table 2 compares the surface areas of the samples as determined by the BET method. Surface areas of Li–$ZrSiO_4$ samples did not vary with irradiation, thus, showing that these compounds are also texturally stable. The $Li_2ZrSi_6O_{15}$ surface area decreased from 9.2 to 3.1 $m^2\ g^{-1}$. This change in the surface area may be due to the changes in the composition of the sample as well to a different morphology.

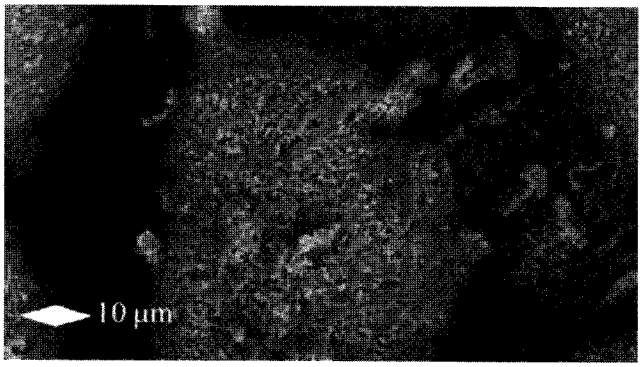

Fig. 4. SEM micrograph of Li–$ZrSiO_4$ powders with Li : Zr molar ratio of 1 : 1, before irradiation.

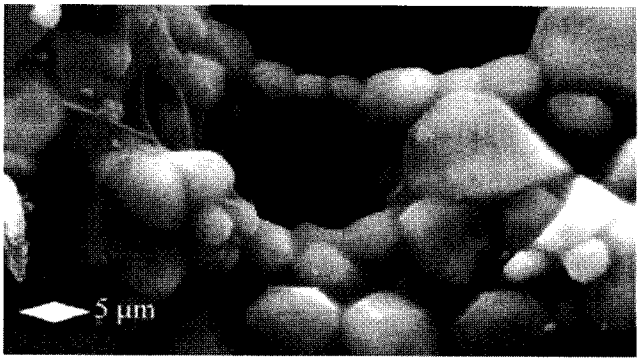

Fig. 5. SEM micrograph of $Li_2ZrSi_6O_{15}$ powders before irradiation.

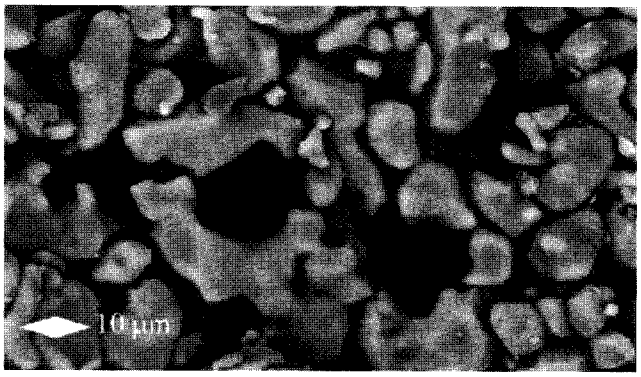

Fig. 6. SEM micrograph of $Li_2ZrSi_6O_{15}$ powders after irradiation.

The morphology of Li–$ZrSiO_4$ before and after the irradiation was laminar and smooth as shown by SEM (Fig. 4). However, Li–$ZrSiO_4$ samples, after irradiation, were smoother than Li–$ZrSiO_4$ samples before irradiation. The micrographs of $Li_2ZrSi_6O_{15}$ showed differences in the morphology before and after the irradiation (Figs. 5 and 6). The micrograph obtained for $Li_2ZrSi_6O_{15}$ before irradiation shows chains of particles, forming circles (Fig. 5). A radiation effect on the morphology is clear in Fig. 6. The particles present a consolidation effect similar to that observed by Yang et al., when studying lithium silicates [26]. This effect is due to the mixed radiation field. Furthermore, this result may explain the decrease of the surface area.

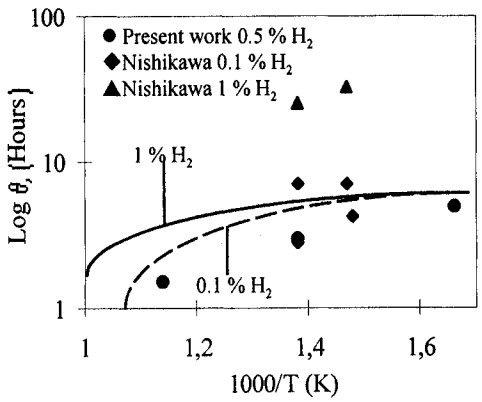

Fig. 7. Comparison of estimated values of total residence time with observed residence time from different experiments.

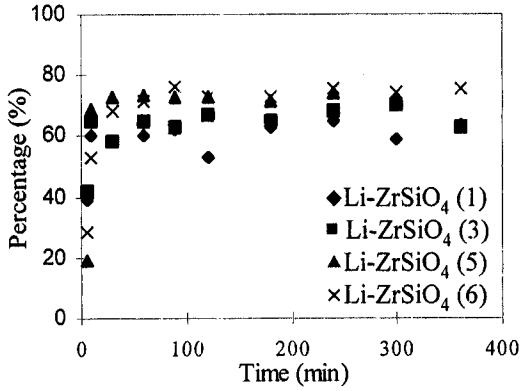

Fig. 8. Tritium release as a function of time, for the Li–$ZrSiO_4$ samples with Li : Zr molar ratios of 1, 3, 5 and 6.

3.2. Tritium release

Nishikawa et al. [28] developed different experiments and a theoretical model for the total tritium residence time (θ_{total}) in lithium metazirconate (Li_2ZrO_3). Fig. 7 compares the Nishikawas's results with the results obtained in this work. The experimental values obtained in this work are located under the theoretical curves, most probably because the theoretical model considers the presence of water in the sweep gas. In this work, the sweep gas did not contain water, then, the theoretical model has to be modified and the resulting curve would be closer to the experimental values.

Fig. 8 shows the tritium release evolution with time for the Li–$ZrSiO_4$ samples with Li : Zr molar ratios of 1, 3, 5 and 6. All samples, at equilibrium, released between 60 and 76% of tritium. The tritium release at equilibrium increased when the Li : Zr molar ratio increased. An explanation of this behaviour is related to the vacancies and interstitial positions in the Li–$ZrSiO_4$ samples. The presence of vacancies could have inhibited diffusion and release, as the tritium atoms may be trapped in these positions. Hence, if the $ZrSiO_4$ structure is saturated with lithium atoms, there are no more vacancies available in the structure, and tritium diffusion and release become easier.

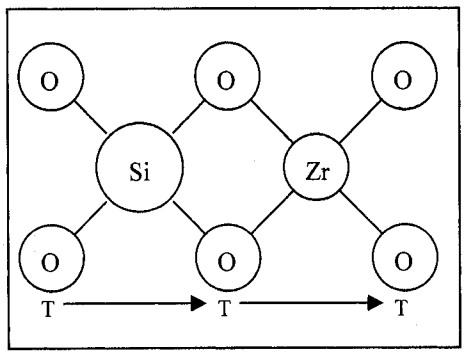

Fig. 9. The migration path found for the tritium interstitial to move through the material. Tritium atom is denoted by a T.

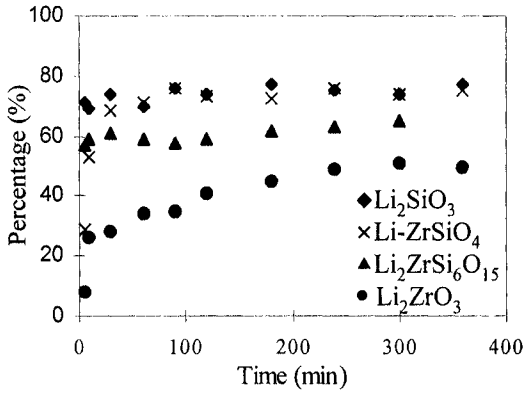

Fig. 10. Tritium release as a function of time, for the $Li_2ZrSi_6O_{15}$, Li–$ZrSiO_4$ (Li : Zr = 6), Li_2SiO_3 and Li_2ZrO_3 samples.

Irradiated $ZrSiO_4$ may present defects energetically favored in the following order [31]: anion Frenkels, interstitials, Schottky and cation Frenkels. In this case, anion Frenkel defects may not exist as the oxygen in the samples studied in the present work is in excess [21]. Therefore, energetically the most probable kind of defects into the $ZrSiO_4$ are interstitial defects. Then, tritium most probably diffuses as an interstitial atom. This seems to be the easiest diffusion mechanism and it is in agreement with the experimentally proposed location of lithium into the $ZrSiO_4$ lattice [21]. The mechanism is illustrated in Fig. 9. If tritium is interstitially positioned, it is close to a single oxygen ion forming an O–T bond. Shah et al. [30] have shown that the tritium atom can move freely around the oxygen ion and it moves into the material jumping from one oxygen atom to the other. Furthermore, $ZrSiO_4$ structure presents channels, and these channels are surrounded mainly by oxygen and some silicon atoms [21,32]. Hence, tritium atoms are expected to diffuse interstitially following these channels.

Fig. 10 shows the tritium release of various lithium compounds for comparative purposes: Li_2SiO_3, Li_2ZrO_3, $Li_2ZrSi_6O_{15}$ and Li–$ZrSiO_4$ whose tritium release was the best one (Fig. 9) is also presented in Fig. 10. The samples, at equilibrium, released an amount of tritium between 45 and 78%.

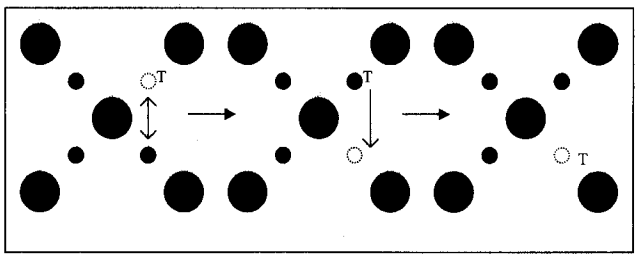

Fig. 11. Possible pathway for a vacancy diffusion. Oxygen atoms are denoted by black and big circles, lithium atoms are denoted by black and small circles, tritium atom is denoted by a T and vacancy is denoted as a small and open circle.

Li_2SiO_3 and Li_2ZrO_3, studied in this work for comparative purposes, were in agreement with those reported in the literature [10,11,14,28]. Li_2ZrO_3 presented a moderate tritium diffusion (45%). Furthermore, the rate of tritium release from Li_2ZrO_3 was different than that obtained from the other compounds. Its rate of release of tritium was slower, the equilibrium being obtained in 300 min. This behaviour may be due to the packed structure of Li_2ZrO_3 if compared with the other compounds. On the other hand, Li_2SiO_3 presented a good tritium diffusion (78%).

On the other hand, $Li_2ZrSi_6O_{15}$ presented a moderate tritium release (60%). In this sample, the diffusion mechanism is expected to be different from the one discussed above for Li–$ZrSiO_4$. $Li_2ZrSi_6O_{15}$ presents defects such as, vacancies, radicals and impurities like SiO_2 and ZrO_2 into the sample. Hence, the diffusion takes place by a vacancy mechanism. Abramenkovs et al. [29] found that radiation defects influences tritium localization processes in a lithium silicated matrix during neutron irradiation. On the surface, tritium localizes with the formation of chemical bonds ≡Si–O–T and ≡Si–T among others. Then, tritium may be anchored with these radicals, therefore, diffusion becomes slow. Reactions (1) and (2) show two examples of this kind of situations:

$$T^0 + {\equiv}Si\text{–}O^0 \rightarrow {\equiv}Si\text{–}O\text{–}T, \quad (1)$$

$$Si^0 + T^0 \rightarrow {\equiv}Si\text{–}T. \quad (2)$$

According to Shah [30], the easiest vacancy mechanism only requires a tritium atom and a vacancy which move swamping positions (Fig. 11). Then, the presence of radicals and impurities like SiO_2 and ZrO_2 must inhibit tritium diffusion and release into the $Li_2ZrSi_6O_{15}$ lattice.

The best tritium release under these conditions was obtained in Li_2SiO_3 and Li–$ZrSiO_4$ (Li : Zr = 6) samples. In these compounds, the total tritium released were 78 and 76%, respectively. Last but not least, Li–$ZrSiO_4$ (Li : Zr = 6) is a thermally and physicochemically stable material [18–20], therefore, it fulfills the two main requirements to be used as a breeder material.

4. Conclusions

The characterization techniques showed that the Li–$ZrSiO_4$ samples were very stable under irradiation. They did not present any change in their composition, morphology or structure. The $Li_2ZrSi_6O_{15}$ was structurally modified by irradiation, as following a radiolysis reaction, the SiO_2 and ZrO_2 contents increased. Furthermore, while the morphology changed, the surface area decreased. This is due to the consolidation process produced by the mixed radiation field.

Tritium release from Li–$ZrSiO_4$ sample with a Li : Zr molar ratio of 6 was similar to the tritium release from Li_2SiO_3, which is considered one of the most promising tritium breeder materials to be used in fusion reactors. Furthermore, according to our results and those reported in the literature, $ZrSiO_4$ is physicochemically and thermally stable at high temperatures. Therefore, Li–$ZrSiO_4$ can be considered a good candidate to be employed as a breeder ceramic material. On the other hand, $Li_2ZrSi_6O_{15}$ presented a moderate tritium release, but unfortunately it was damaged by irradiation. Finally, tritium follows different diffusion mechanisms into the Li–$ZrSiO_4$ and the $Li_2ZrSi_6O_{15}$. Tritium into the Li–$ZrSiO_4$ lattice follows an interstitial diffusion mechanism while into the $Li_2ZrSi_6O_{15}$ lattice it follows a vacancy diffusion mechanism.

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