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Study of Lithium Germanate Additions to Advanced Ceramic Breeder Pebbles

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Abstract

Worldwide, lithium rich ceramic pebbles are being developed to be used as tritium breeders inside future fusion reactors. Upon irradiation, the pebbles will produce tritium which will be used alongside deuterium to fuel the fusion reaction. It is essential that these pebbles are of sufficient quality to withstand the various forces experienced within the wall of the reactor. Currently, a melt-based process is used at the Karlsruhe Institute of Technology for the production of pebbles composed of lithium orthosilicate with a secondary strengthening phase of lithium metatitanate. Recent studies have focused on incorporating lithium orthogermanate. Various compositions were used to perform fundamental studies to determine phase transitions as well as melting points for processing. The melt-based KALOS process was then used to produce pebbles with selected compositions, after which the pebbles underwent a series of characterisation tests. Additionally, pebbles were held at reactor relevant temperatures to determine any changes to the mechanical strength. It was found that pebbles with 30 mol% lithium metatitanate and a lithium orthosilicate/orthogermanate ratio in the range of 1.5 - 4 showed an increased strength as well as good thermal stability and may have the potential to be used as tritium breeders.

Introduction

In order for future fusion reactors to be a major contributor to the generation of world wide electricity, they will need a reliable and adequately large supply of their two fuel components on-site [1]. While deuterium is readily extracted from sea water and suitable for storage, the prevalence of tritium on earth is too low for efficient extraction. Furthermore, due to its quick radioactive decay tritium can also not be stored effectively for long periods of time. It is therefore intended to breed tritium within the reactor by the transmutation of lithium atoms upon neutron irradiation from the fusion reaction. In order to be self-sufficient, a future fusion reactor has to make sure that, all in all, every generated neutron transmutes one lithium atom, if no tritium atom is lost in its handling. In the case of the European Helium Cooled Pebble Bed (HCPB) breeding blanket, lithium rich ceramic pebbles are to be featured in the wall of the fusion reactor (the so-called blanket) in the form of pebble beds [2]. In order to enhance the probability of tritium generation (or in other terms the generation of tritium per neutron, i.e. the tritium breeding ratio - TBR), the pebbles will need to be enriched with ^6Li [3]. Additionally, a section of neutron multipliers, e.g. beryllium pebbles, will also be included in the breeding blanket to increase the chance that lithium atoms will be hit by neutrons and transmute to tritium (and helium as a by-product).

The tritium is to be continuously extracted from the beds, processed and re-routed into the reactor. It is imperative that these pebbles are of sufficient quality to be able to withstand various forces including thermal forces, mechanical forces due to varying thermal expansions as well as the neutron flux from the plasma.

Currently at the Karlsruhe Institute of Technology, lithium orthosilicate (Li_4SiO_4 , LOS) based ceramic pebbles are produced using the melt-based KALOS process [4]. A melt-based process was chosen over other processing methods due to the ease at which used material can be reprocessed after use in the reactor without any wet chemical (re-)processing [5]. Recently, bi-phasic advanced ceramic tritium breeders have been developed containing lithium metatitanate (Li_2TiO_3 , LMT) as a secondary phase, which results in an increase in the mechanical strength and long-term stability of the pebbles as well as limiting the grain growth [6,7]. Recent studies have focused on incorporating a third component, namely lithium orthogermanate (Li_4GeO_4 , LOG) to investigate the possible influence on material properties and phase transitions. LOG may also be an advantageous addition, as the amount of silicon in the pebbles is reduced, thereby decreasing the long-term activation by the long-life ^{26}Al isotope formed upon neutron irradiation [8].

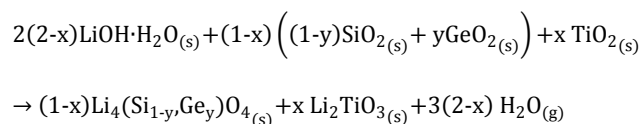
Previous studies on the LOG-LOS system have shown that a complete, yet polymorphic solid solution exists in the binary system, which can either be in the monoclinic or orthorhombic form depending on the temperature and the Ge/Si ratio [9]. It was found that the transition from the high-LOS to low-LOG structure (monoclinic – orthorhombic) at about 710 °C (upon cooling) rapidly decreases in temperature with increasing LOS content and approaches ambient temperature at about 55 mol% LOS. On the other side, the two second-order transitions of LOS observed at 665 and 723 °C [10] fall gradually to lower temperatures with increasing LOG content until they intersect with the phase transition of LOG [9] (see also following Fig. 3).

In terms of processing, LOG has a melting point of 1280 °C [11], which is quite similar to the melting point of LOS at 1258 °C [12]. LOG has a lithium density similar to LOS and higher than that of LMT, meaning any additions of LOG will not significantly alter the lithium density, which is important for maintaining the TBR. Yet, it is expected that additions of LOG will have an effect on the second-order transitions of LOS and may also have an impact on the mechanical properties of the pebbles. But then it is also expected that additions of LMT will influence the melting temperature and phase transitions in the LOG-LOS system. For the later use of the breeder material, any phase transition taking place in the operating temperature range of the blanket should be carefully considered as these might be detrimental to the mechanical strength of the pebbles. This can result in the fracturing of the pebbles, causing dust formation and the caking of the purge gas system, leading to an inadequate tritium extraction rate.

Experimental

In order to investigate the LOG-LOS system as well as the effects of adding LMT to the LOG-LOS system, first a series of powder mixtures were prepared. LiOH·H₂O (Alfa Aesar 98 %), SiO₂ (Alfa Aesar 99.5 %, metal basis), GeO₂ (Alfa Aesar 99.999 %, metal basis) and optionally TiO₂ (Alfa Aesar 99.8 %, metal basis) were stoichiometrically mixed together to form compositions with 0, 20 and 30 mol% LMT and a wide range of LOG contents. A solid-state reaction method was then used for synthesis.

For the production of pebbles, the synthesis powders were heated to 150 °C to remove the hydrate water in a preparatory step. Next, the powders were pre-reacted at 470 °C for 3 hours to form the anticipated phases LOG-LOS and LMT. The following equation details the complete reaction:



The reacted powder was then filled into a platinum alloy crucible and heated to approximately 1350 °C (or about 80 K above the melting point) to form a melt. A pressure was applied to the crucible to force the melt through a 500 µm nozzle, forming a laminar jet. Instabilities on the surface of the jet caused droplets to break off, which were subsequently solidified in a cooling tower below the oven using liquid nitrogen. The pebbles were collected at the base of the tower and stored in a dry and inert atmosphere until the characterisation techniques were performed.

A series of characterisation methods were used to examine the prepared powder compositions and pebbles. Differential scanning calorimetry (DSC) (Netzsch-STA 449C-Jupiter) was performed on selected samples to evaluate the temperatures of phase transitions and melting. (A rate of 5 K/min was chosen for heating, while for cooling a rate of 20 K/min was necessary to observe the small reactions enthalpies of the phase transitions.) X-ray diffraction (XRD) (Bruker D5005) was used for phase analysis. The qualitative phase analysis was performed on the basis of the ICDD PDF-2 2010 database. Additionally, a Rietveld refinement by a fundamental parameters approach was applied using Bruker.AXS TOPAS v6 to determine the lattice parameters of lithium orthosilicate, lithium orthogermanate and lithium metatitanate on the basis of the crystal structure that were published by Deng et al. [13] for Li₄SiO₄, Kataoka et al. [14] for β-Li₂TiO₃ and Laumann et al. [15] for γ-Li₂TiO₃ as well as Völlenknecht et al. [16] for Li₄GeO₄. The surfaces of the pebbles, as well as polished and etched cross-sections of embedded pebbles were examined by scanning electron microscopy (Zeiss Supra 55) and element mappings on cross-sections were performed by energy dispersive X-ray microanalysis (EDAX Apollo-40). To evaluate the mechanical properties, uniaxial compression tests (so-called crush-load tests) were performed on each batch of produced pebbles (ZwickiLine 5kN). Pebbles with diameters of 1000 µm were tested for each composition, which involved compressing 40 individual pebbles until they fractured. The average force required to cause the fracture was then determined for each sample. In order to test the stability of the pebbles at reactor relevant temperatures, selected pebble samples were additionally annealed at 900 °C for 3 weeks, after which the crush-load tests were repeated.

In the following, the sample compositions are consequently expressed in molar proportions (mol%) of lithium orthosilicate (LOS), lithium metatitanate (LMT) and lithium orthogermanate (LOG). In cases where results of compositions containing 20 or 30 mol% LMT are compared to those without LMT, the LOS and LOG contents were 'normalised', i.e. the LOS and LOG proportions were recalculated to a LMT free composition.

Results and Discussion

To evaluate the melting and transition temperatures, DSC analysis was performed on several compositions. Figure 1 exemplarily shows the DSC signals for the composition 40 mol% LOG and 60 mol% LOS. For all samples, the peak temperatures upon heating for the endothermic melting and upon cooling for the exothermic phase transitions were determined. It was observed that not only the transition temperatures of the second order transition in the LOS phase is decreased with increasing LOG content, but also the DSC signals, and thus the reaction enthalpies during the transitions in the LOS phase, decrease with increasing LOG content (Fig. 2).

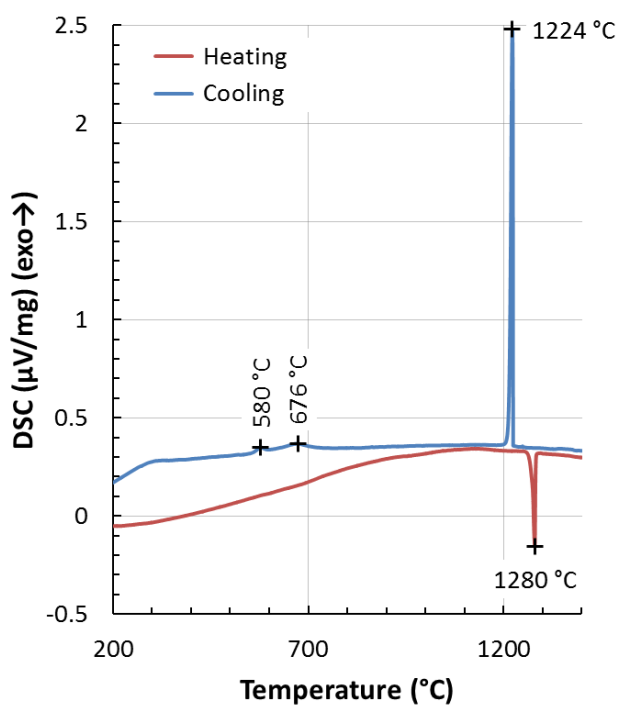


Figure 1: DSC graph for the composition of 40 mol% LOG and 60 mol% LOS.

The determined phase transitions are shown in Fig. 3. Data from [9] and [10] were used for pure LOG and LOS, respectively. The measured data points for the phase transitions in the LOG-LOS system agree quite well with those of [9] considering that our data were obtained during cooling with a rate of 20 K/min. In combination with the XRD results (see Table 1), it was possible to determine whether the solid solution of

LOS and LOG was in the orthorhombic or in the monoclinic form. Below a normalised LOS content of about 55 mol%, the phase will be in the orthorhombic form at room temperature. As the temperature increases, the crystal structure will eventually change to monoclinic, whereby increasing the LOG content raises the transition temperature to 710 °C (upon cooling) in pure LOG [9]. Similar to the phase transitions in the LOS structure (Fig. 2), it was observed that the reaction enthalpy of the phase transition from the LOS to the LOG structure is decreased with decreasing temperature, i.e. in this case with increasing LOS content. Yet, the reaction enthalpies are higher than those of the phase transitions in the LOS structure displayed in Fig. 2.

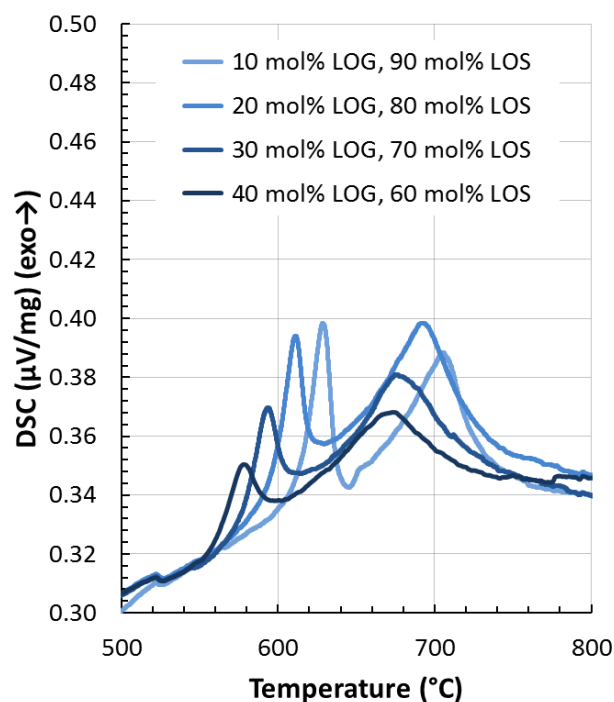


Figure 2: Details of DSC graphs during cooling for different compositions between 10 and 40 mol% LOG (balance LOS), displaying the temperature region of the second order transitions in the LOS phase.

Above a normalised LOS content of about 55 mol%, the solid solution is always in the monoclinic phase. When increasing the temperature, these compositions will experience two second-order transitions that were detected at 665 °C and 723 °C for pure LOS [10]. It was observed that the addition of LMT lowers the phase transition temperatures in the LOG as well as in the LOS structure only by about 10 – 20 K (not displayed in Fig. 3).

The determined melting points are shown in Fig. 4. Here the normalised LOS content was used so that results of samples with additions of 20 and 30 mol% LMT can also be included in the diagram. Data from [11] was used for pure LOG, while data from [12] was included for pure LOS. It is obvious that the ratio of

LOS to LOG has a relatively small effect on the melting temperature and hence on the temperature to be used for the later melt-based processing. The determined melting temperatures are overestimated compared to the literature data, because the peak temperature upon heating was used (compare Fig. 1). The addition of 20 or 30 mol% LMT causes a reduction in the melting temperature of approximately 70 K for the selected LOG-LOS compositions.

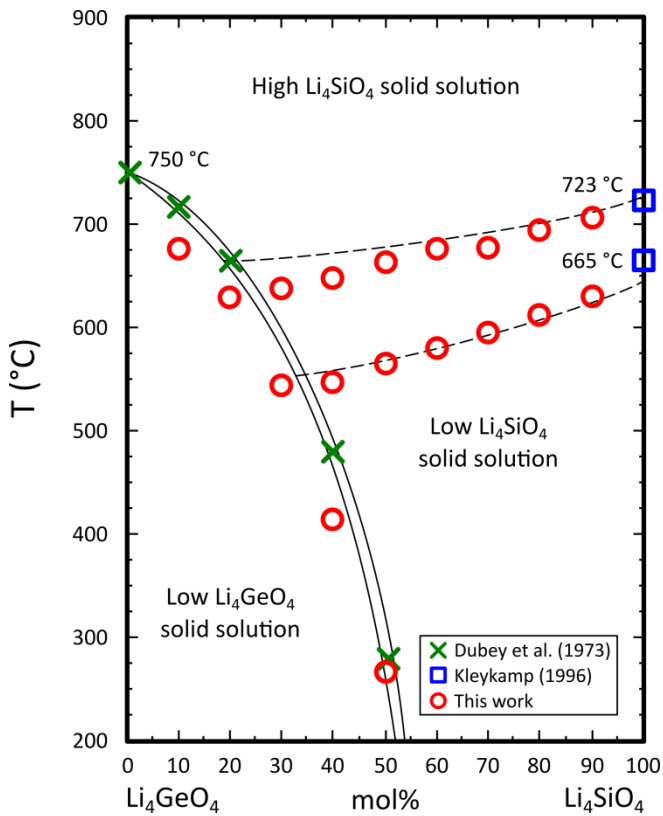


Figure 3: Phase transitions in LOG-LOS solid solutions compared with literature data from Dubey et al. [9] and Kleykamp [10].

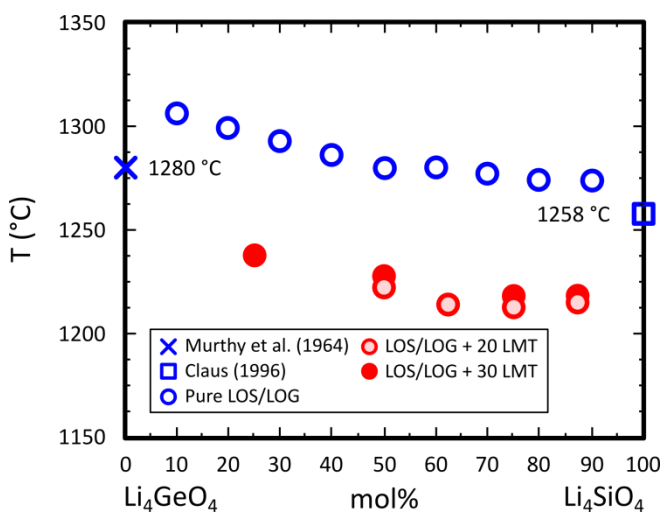


Figure 4: Melting points for LOG-LOS solid solutions and with additions of 20 and 30 mol% LMT. Published data from Murthy and Ip [11] and Claus et al. [12] are given as reference points.

With the ascertained melting temperatures, several compositions were selected for the fabrication of pebbles by the melt-based KALOS process. The size of the pebbles is pre-dominantly determined by the break-up of the melt jet. In general, the main droplet size is approximately twice the diameter of the jet as determined by the Rayleigh break-up of the jet [17]. A 500 μm nozzle was used for the production, resulting in a main pebble size of approximately 1000 μm , which corresponds well to the sizes of the pebbles obtained in the produced batches (assuming only minor size changes upon solidification). The smaller pebbles are produced either due to the break-up of larger droplets under shear stress or as the result of satellite droplets between the main droplets [18, 19]. Larger pebbles may be formed by the agglomeration of droplets.

In Figure 5, pebbles with 20 mol% LMT and varying LOG-LOS contents are displayed. The pebble batch with a normalised LOS content of 50 mol% reveals a high amount of fractured pebbles (Fig. 5a). While especially the pebbles with a normalised LOS content of 62.5 mol% (Fig. 5b), but also those with a normalised content of 87.5 mol% LOS (Fig. 5d) exhibit a lot of cracks, the pebbles with a normalised LOS content of 75 mol% show less surface defects (Fig. 5c). During cooling, all these compositions experienced the high-low phase transitions in the LOS structure, but only the composition with a normalised LOS content of 50 mol% additionally underwent the transition from the high LOS to the LOG structure at quite low temperatures.

Figure 6 shows the surface morphology of pebbles containing four different normalised LOS contents with a constant LMT content of 30 mol%. The sample in Fig. 6a with a normalised content of 25 mol% LOS exhibits cracks at the surface as well as some fractured pebbles. During cooling, the crystal structure changes from monoclinic to orthorhombic, probably resulting in internal stresses within the pebble, which end up causing the defects and fractures. Also the sample in Fig. 6b displays a high amount of cracks and defects as well as some pebble fragments. It contains a normalised LOS content of 50 mol%, which lies on the phase transition line between orthorhombic and monoclinic, presumably causing these defects. The most robust looking pebbles are seen in Fig 6c with a normalised LOS content of 62.5 mol%. According to the phase diagram in Fig. 3, these samples remained in the monoclinic phase upon cooling. The pebbles with a normalised content of 87.5 mol% LOS in Fig. 6d experienced a

similar transition history, yet they display a higher amount of defects and cracks.

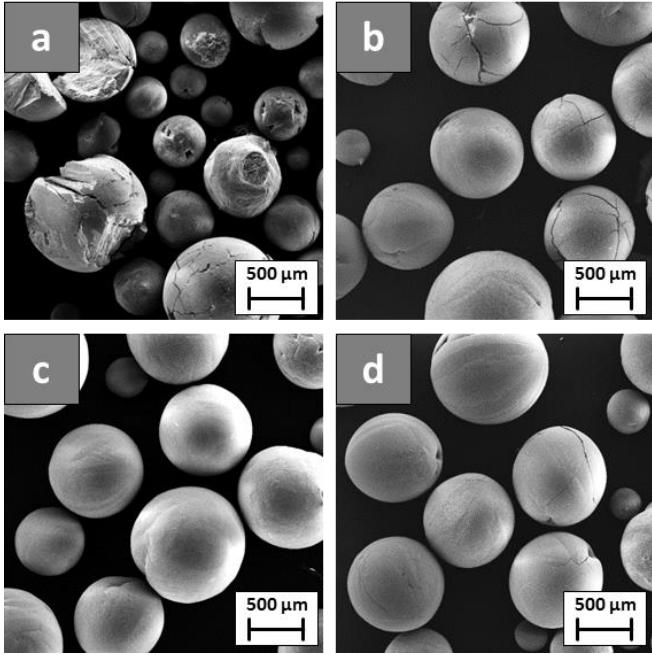


Figure 5: Surface morphology of pebbles containing 20 mol% LMT and a normalised LOS content of a) 50 mol%, b) 62.5 mol%, c) 75 mol% and d) 87.5 mol%.

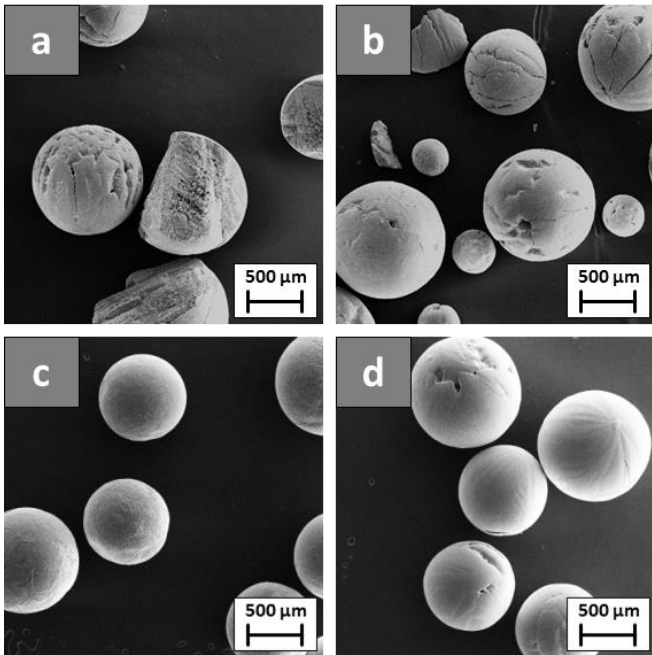


Figure 6: Surface morphology of samples containing 30 mol% LMT and a normalised LOS content of a) 25 mol%, b) 50 mol%, c) 62.5 mol% and d) 87.5 mol%.

Figure 7 shows the chemically etched pebble microstructure of samples containing a normalised LOS content of 75 mol% with both 20 and 30 mol% LMT, respectively. The microstructures reveal the darker LOG-LOS solid solution as well as the lighter LMT phase. For pebbles with 20 mol% LMT in Fig. 7a, the LOG-LOS phase is the first to crystallise and this is assumed to be due to an eutectic observed between 20 and 30 mol% LMT in the LOS-LMT system [7]. An

effect of the LOG on the presence of this eutectic was not observed. The LMT fills in the gaps between the dominant LOG-LOS structures. When the LMT content increases beyond the eutectic composition, it will crystallise first, resulting in the LMT dendrites dominating the microstructure, surrounded by the solid solution of LOG-LOS as can be seen in Fig. 7b.

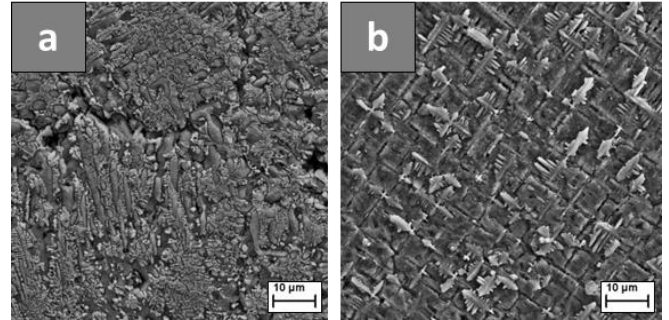


Figure 7: Microstructure of pebbles containing a normalised LOS content of 75 mol% and a) 20 and b) 30 mol% LMT.

In Figure 8 a SEM image of the microstructure for a non-etched 30 mol% LMT pebble sample containing a normalised LOS content of 75 mol% is displayed in comparison to the element mappings of Ti, Ge and Si. The titanium is clearly visible, representing the dendritic structure of the LMT phase. There is a fine dispersion of silicon and germanium throughout the solid solution which fills the volume between the dendrites. Additionally, it can be seen that there is no mixing between the phases, resulting in clearly defined areas of the LOG-LOS solid solution and the LMT phase.

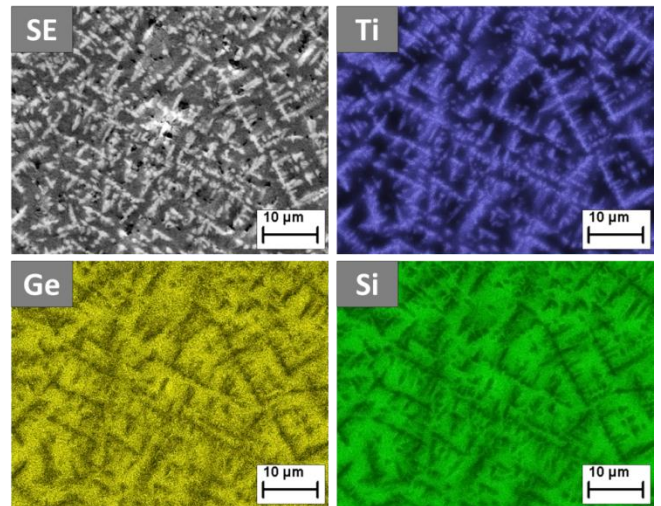


Figure 8: Microstructure and element mappings of Si, Ge and Ti for a pebble containing a normalised LOS content of 75 mol% and 30 mol% LMT.

In Table 1 the determined phase content of the fabricated pebble samples is shown as well as of those annealed at 900 °C for 3 days. For high LOG contents (up to 50 mol%), the pebbles exhibit the orthorhombic LOG structure and γ -LMT in the as-

fabricated state or β -LMT in the annealed state. For high LOS contents (62.5 mol% and more), the samples show the monoclinic LOS structure and γ -LMT or β -LMT. These findings are in accordance with the phase diagram of the LOG-LOS solid solution by Dubey et al. [9] as well as Fig. 3. The presence of γ -LMT in the as-fabricated state is in agreement with previous findings that the high temperature γ -modification of LMT is conserved because of the rapid quenching in the melt-based fabrication [7]. Yet surprisingly the 20 mol% LMT containing pebbles with normalised LOS contents of 62.5 and 75 mol% feature the LOS as well as the LOG solid solution structure together with LMT. Table 1 also shows that the annealing of the pebbles eventually leads to the transformation of the LOG solid solution to the LOS structure as expected from the phase diagram. From this observation it is clear that fluctuations in the composition, which may arise from the production process and could have led to two types of pebbles with different germanium contents, cannot explain the presence of both solid solution phases. It can therefore be deduced that the rapid quenching of the pebbles during fabrication leads to the metastable freezing of a fraction of the LOG-LOS solid solution in the orthorhombic LOG structure. Whether the individual pebbles actually feature these three phases simultaneously or whether the pebbles feature either the LOS structure or the LOG structure cannot be determined from these results. It is, however, also apparent that the samples with a content of 30 mol% LMT do not show three

phases. As displayed in Figure 7, the microstructure of the pebbles is determined by the LMT content and the sequence of the crystallisation of the phases. Nevertheless, it has to be assumed that in all cases, the LOG-LOS solid solutions will solidify in the high-temperature LOS structure, just at different temperatures. The reason, why the low LOG structure is formed only in the pebbles with 20 mol% LMT and relatively high normalised LOS contents of 62.5 and 75 mol%, cannot be deduced from the present results. There may be local fluctuations in the LOG-LOS composition within the single pebbles or the LOG structure may be preferred for kinetic reasons during quenching.

In Figure 9 the unit cell volume of selected samples is detailed as a function of the normalised LOS content. It can be seen, that the unit cell volume of each structure follows a linear trend, i.e. Vegard's law apparently applies to this system [20]. This is also true for the samples that show the LOS structure as well as the LOG structure, which is a clear indication that these samples do not suffer from a heterogeneous distribution of the elements. It is also evident, that the annealing of the samples does not have a considerable effect on the unit cell volume, although there seems to be a tendency towards slightly lower unit cell volumes, which can hint at the annealing of intrinsic stresses. Also the phase transition from orthorhombic LOG to monoclinic LOS that is observed e.g. in the 75 mol% LOS and 20 mol% LMT containing

Table 1: Determined phases from the XRD measurements and their qualitative phase content are given for various samples. LOG and LOS denote the crystal structure of the present solid solution (major phase: ●, second phase: ◐, minor phase: ○).

Normalised LOS content (mol%)	LMT content (mol%)	status	LOS	LMT	LOG
25	30	as-fabricated		◐	●
		annealed		◐	●
50	20	as-fabricated		◐	●
		annealed		◐	●
	30	as-fabricated		◐	●
		annealed		◐	●
62.5	20	as-fabricated	●	◐	○
		annealed	●	◐	
	30	as-fabricated	●	◐	
75	20	as-fabricated	●	◐	○
		annealed	●	◐	
	30	as-fabricated	●	◐	
		annealed	●	◐	
87.5	20	as-fabricated	●	◐	
	30	as-fabricated	●	◐	

sample (see Table 1), does not lead to considerable deviations from the unit cell volume of the as-fabricated pebbles.

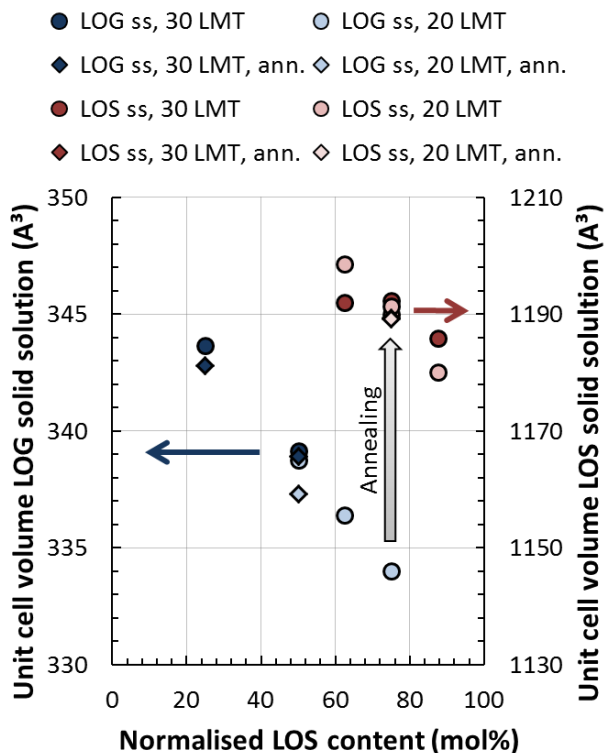


Figure 9: The determined unit cell volume of LOG and/or LOS solid solutions (“ss”) as a function of the normalised LOS content. The samples with 20 or 30 mol% LMT were measured as-fabricated or in the annealed state (“ann.”).

The effect of the LOG content on the mechanical strength measured as the average crush-load of the pebbles is shown in Figure 10. The diagram also evidences the effect of increasing the LMT content from 20 to 30 mol%, which is known to increase the mechanical strength of pebbles containing only LOS and LMT [6, 7]. In general, the LOG-LOS pebbles with 20 LMT hardly display any improvement compared to pebbles composed of solely LOS and LMT, only in the case of 30 LMT an enhancement can be achieved. A maximum in the crush load occurs at a normalised LOS content of 62.5 mol% for the 30 LMT pebbles, while the maximum for 20 LMT is obtained at a normalised LOS content of 75 mol%.

As the ratio between LOG and LOS becomes equal, the strength of the pebbles greatly diminishes. At a normalised LOS content of 50 mol%, the pebbles on average cannot withstand even a force of 5 N. As the normalised LOS content falls below 50 mol%, the strength of the pebbles slightly increases again, but does not quite reach the levels seen above 50 mol%. At large the results correspond quite well with the observations of the pebble appearance in figs. 5+6.

In order to simulate the thermal effects in the breeding blanket, different compositions were selected to undergo a heat treatment at approximately the maximum temperature expected within the breeding blanket of 900 °C. It was observed that the pebble samples remain quite stable and exhibit no or only a slight reduction in the average crush-load values (0-4 %). Only the sample with a normalised content of 25 mol% LOS and 30 mol% LMT displayed a severe reduction of the average crush-load of about 60 %.

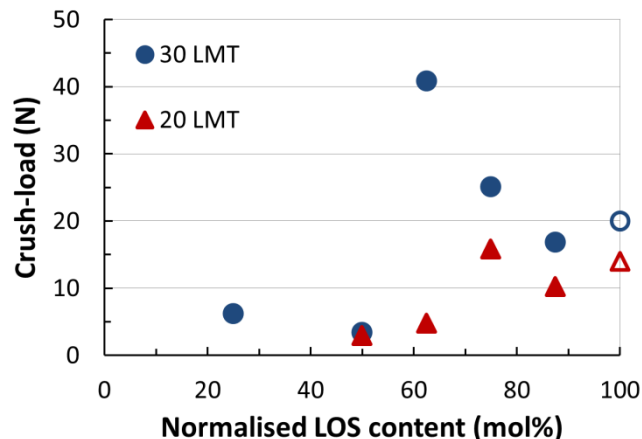


Figure 10: Effect of the normalised LOS content on the mechanical strength of pebbles with a diameter of 1000 μm . (The data for pebbles without LOG are taken from [6, 7].)

Hardly anything is known about the mechanical properties of solid solutions in the LOG-LOS system in spite of the fact that these compositions, also with various dopants, were widely investigated as solid electrolytes for their good ionic conductivity. Only in [21] it is mentioned that a composition with 33 mol% LOS exhibited a loss of strength when passing through the phase transition during cooling. Although the rapid quenching of the melt-based fabrication process makes high and even unusual demands on the material compared to e.g. a sintering process, it can be concluded from our results that the phase transition from the LOS structure to the LOG structure is detrimental to the mechanical strength, and that for application as breeder materials compositions that exhibit this phase transition, i.e. LOS contents ≤ 55 mol%, should be avoided, especially if the transition temperature falls inside the operating temperature range (approx. 500 – 900 °C). Even if there seems to be a slight increase in the crush-load when decreasing the LOS content from 50 to 25 mol%, the annealing of these samples, where they experienced the phase transition again, led to a severe reduction of the mechanical strength. That these pebbles do not feature as severe defects as the pebbles that undergo the phase transition near room temperature (50 mol%

LOS) might be explained by a thermal stress reduction process. At higher temperatures the resultant stresses of the phase transition can very likely be partially dissipated by thermally activated processes, even if the observed reaction enthalpy is larger than near room temperature.

On the LOS rich side of the considered system an obvious increase of the crush-load was detected, especially for pebbles with 30 mol% LMT. The decrease in vigorousness of the high-low transition of LOS with increasing germanate content, which is suggested by the decrease of the reaction enthalpy in the DSC measurements, seems to be beneficial for the resulting mechanical properties. That the increase of the crush-load for pebbles with 20 mol% LMT in this LOS range could not or insignificantly be detected might be explained by the unexpected presence of the undercooled LOG solid solution. This phase certainly results from the rapid quenching of the melt-based process, so that differently fabricated samples might also show an increase of the mechanical strength in this composition range.

Summary

Lithium rich ceramic pebbles made of lithium orthosilicate and lithium metatitanate were successfully fabricated with additions of lithium orthogermanate, which forms a solid solution with lithium orthosilicate. This solid solution phase may either crystallise in the lithium orthogermanate structure or the lithium orthosilicate structure, depending on the germanium content. Characterisation of the fine-grained microstructure showed that the solid solution between lithium orthosilicate and lithium orthogermanate does not mix with lithium metatitanate, which is added as a strengthening phase. Due to the phase transition from the monoclinic LOS to the orthorhombic LOG structure that occurs during the fabrication, pebbles

with a normalised LOS content of 50 mol% and below showed poor mechanical strength, making them prone to fracturing and dust creation. Therefore pebbles with these compositions cannot be recommended for use as tritium breeders. Pebbles with a higher LOS content show a generally higher mechanical strength as well as good thermal stability during annealing, especially with additions of 30 mol% LMT. Compositions with normalized LOS contents between 60 and 80 mol% might have a considerable potential for use in a fusion reactor. Yet the production of additional batches will be needed to determine the optimum amount of LOG, and the investigation of further properties, such as long-term annealing and tritium release, is required to qualify the material for tritium breeding.

The results also show that under certain fabrication conditions, such as the rapid quenching in the KALOS process, the LOG structure can form in a metastable state to some degree, although the exclusive formation of the LOS structure is expected. Considering the crystal lattice parameters, Vegard's law seems to apply to the present system, including the samples that show the metastable LOG structure. Furthermore, during thermal annealing the expected LOS structure, as well as the expected crystal lattice parameters, are formed. The actual mechanism for the formation of the metastable LOG structure is still unclear.

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References

- [1] Haarms, A. A., et al., Principles of Fusion Energy: An Introduction to Fusion Energy for Students of Science and Engineering. World Scientific Publishing Co. Pte. Ltd., Singapore, 2000
- [2] Hernández, F.A., Overview of the HCPB Research Activities in EUROfusion. IEEE T. Plasma. Sci. 46 (2018) 2247-2261.
- [3] Raffray, A.R., et al. Breeding blanket concepts for fusion and materials requirements, J. Nucl. Mater. 307-311 (2002) 21-30.
- [4] Kolb, M.H.H., et al., Enhanced fabrication process for lithium orthosilicate pebbles as breeding material, Fusion Eng. Des. 86 (2011) 2148-2151.
- [5] Leys, O., et al., The reprocessing of advanced mixed lithium orthosilicate/metatitanate tritium breeder pebbles. Fusion Eng. Des. 107 (2016) 70-74.
- [6] Knitter, R., et al., Fabrication of modified lithium orthosilicate pebbles by additions of titania, J. Nucl. Mater. 442 (2013) S433-S436.
- [7] Heuser, J. M., et al., Long-term thermal stability of two-phased lithium orthosilicate/metatitanate Ceramics, J. Nucl. Mater. 507 (2018) 396-402.

- [8] Mukai, K., et al., Activation calculations for multiple recycling of breeder ceramics by melt processing. *Fusion Eng. Des.* 100 (2015) 565-570.
- [9] Dubey, B. L., West, A. R. Crystal Chemistry of Li_4XO_4 Phases: X = Si, Ge, Ti. *J. Inorg. Nucl. Chem.* 35 (1973) 3713-3717.
- [10] Kleykamp, H. Enthalpy, Heat Capacity, Second-order Transitions and Enthalpy of Fusion of Li_4SiO_4 by High-temperature Calorimetry. *Thermochim. Acta.* 287 (1996) 191-201.
- [11] Murthy, M.K., Ip, J. Studies in Germanium Oxide Systems: I, Phase Equilibria in the System $\text{Li}_2\text{O}-\text{GeO}_2$. *J. Am. Ceram. Soc.* 1964, Vol. 47, pp. 328-331.
- [12] Claus, S., et al., Phase Equilibria in the Li_4SiO_4 - Li_2SiO_3 Region of the Pseudobinary $\text{Li}_2\text{O}-\text{SiO}_2$ System. *J. Nucl. Mater.* 230 (1996) 8-11.
- [13] Deng, Yue, et al., Structural and Mechanistic Insights into Fast Lithium-Ion Conduction in Li_4SiO_4 - Li_3PO_4 Solid Electrolytes. *J. Am. Chem. Soc.* 137 (2015) 9136-9145.
- [14] Kataoka, Kunimitsu, et al., Crystal growth and structure refinement of monoclinic Li_2TiO_3 . *Mater. Res. Bull.* 44 (2009) 168-172.
- [15] Laumann, Andreas, et al., Lithium Migration at High Temperatures in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Studied by neutron diffraction. *Chem. Mater.* 23 (2011) 2753-2759.
- [16] Völlenknecht, H., Wittmann, A. Die Kristallstruktur von Li_4GeO_4 . *Z. Krist.* 128 (1969) 66-71.
- [17] Lord Rayleigh, S.J.W., On the instability of jets, *Proc. Lond. Math. Soc.* 10 (1878) 4-13.
- [18] Pilch, M., Erdman, C.A. Use of breakup time data and velocity history data to predict the maximum size of stable fragments for acceleration-induced breakup of a liquid drop. *Int. J. Multiphase Flow.* 13 (1987) 741-757.
- [19] Pimbley, W. T., Lee, H. C. Satellite Droplet Formation in a Liquid Jet. *IBM J. Res. Dev.* 21 (1977) 21-30.
- [20] Vegard, L. Die Konstitution der Mischkristalle und die Raumfüllung der Atome. *Z. Phys.* 5 (1921) 17-26.
- [21] I.M. Hodge, et al., Impedance and modulus spectroscopy of polycrystalline solid electrolytes, *J. Electroanal. Chem.* 74 (1976) 125-143.