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## Abstract

This report deals with the irradiation induced changes of mechanical properties of ceramic breeder materials for fusion reactors. Pellets of $LiAlO_2$, $Li_2O$, $Li_2ZrO_3$, $Li_2SiO_3$, and $Li_4SiO_4$ manufactured by five European laboratories were irradiated in the experiment COMPLIMENT in the epithermal neutron flux of the HFR reactor in Petten (The Netherlands) and in the thermal neutron flux of the OSIRIS reactor in Saclay (France). $Li_2SiO_3$ and $Li_4SiO_4$ pellets made at KfK, Karlsruhe were irradiated in the experiment ELIMA 1 in the fast neutron flux of the KNK-reactor (Karlsruhe). The properties investigated are the ultimate compressive strength and the Young's modulus. A reduction of the compressive strength has been found for all materials. $Li_4SiO_4$ exhibits the largest decrease, the lowest one has been observed in $Li_2ZrO_3$ and $LiAlO_2$. Crack formation is the most effective mechanism in strength reduction. Considering the dependence of the strength reduction on damage doses due to fast neutrons and α- and tritium particles from the $^6Li(n,\alpha)^3H$-reaction, respectively, it is evident that the Li-burnup is the deciding parameter. The relative reduction of the Young's modulus under irradiation is smaller than that of the compressive strength. The Young's modulus depends primarily on the actual values of the density after irradiation.

## Änderungen mechanischer Eigenschaften keramischer Brutmaterialien in den Bestrahlungsexperimenten COMPLIMENT und ELIMA 1

## Zusammenfassung

Der Bericht behandelt die bestrahlungsbedingten Änderungen der mechanischen Eigenschaften keramischer Brutmaterialien für Fusionsreaktoren. Tabletten aus $LiAlO_2$, $Li_2O$, $Li_2ZrO_3$, $Li_2SiO_3$ und $Li_4SiO_4$, die in fünf europäischen Laboratorien herstellt worden waren, wurden im Experiment COMPLIMENT im epithermischen Neutronenfluß des HFR Reaktors in Petten (Niederlande) und im thermischen Neutronenfluß des OSIRIS Reaktors in Saclay (Frankreich) bestrahlt. Im KfK hergestellte $Li_2SiO_3$- und $Li_4SiO_4$-Tabletten wurden im Experiment ELIMA 1 im schnellen Neutronenfluß des KNK-Reaktors (Karlsruhe) bestrahlt. Es wurden die Druckfestigkeit und der E-Modul untersucht. Bei allen Materialien wurde eine Abnahme der Druckfestigkeit beobachtet. Die stärkste wurde bei $Li_4SiO_4$ gefunden, die niedrigste bei $Li_2ZrO_3$ und $LiAlO_2$. Rißbildung ist der wirksamste Mechanismus bei der Festigkeitsabnahme. Betrachtet man die Festigkeitsabnahme als Funktion der Strahlenschäden durch schnelle Neutronen beziehungsweise durch α- und Tritium-Teilchen aus der $^6Li(n,\alpha)^3H$-Reaktion, so zeigt sich, daß der Li-Abbrand der entscheidende Parameter ist. Die relative Abnahme des E-Moduls ist geringer als die der Festigkeit. Der E-Modul ist eine Funktion der Dichte nach Bestrahlung.

# Contents

## 1 Introduction

Within the framework of breeder ceramic development for fusion reactor blankets irradiation experiments with pellets of different candidate materials developed by various European manufacturers have been performed. This report deals with the change of the mechanical properties under irradiation. Results from two irradiation experiments, COMPLIMENT and ELIMA 1, are presented.

In the irradiation experiment COMPLIMENT $LiAlO_2$, $Li_2SiO_3$, $Li_4SiO_4$, $Li_2ZrO_3$, and $LiO_2$ of various European manufacturers have been investigated in two test groups: DELICE 03 and ELIMA 2. In the experiment DELICE 03 the materials have been irradiated in the thermal neutron flux of the OSIRIS reactor in Saclay (France) and in ELIMA 2 in the Cd-screened neutron flux of the HFR reactor in Petten (The Netherlands). The objectives of COMPLIMENT were (1) to study the irradiation behaviour of the different materials under the same test conditions, as neutron fluxes and temperatures, and (2) to compare the radiation damage in the materials caused by fast neutrons with the damage caused by the $\alpha$- and tritium particles from the $^6Li(n,\alpha)^3H$-reaction. The contribution of the $(n,\alpha)$-reaction to the total damage dose is high in the thermal neutron flux of the OSIRIS reactor (DELICE 03) whereas it is relatively low in the epithermal flux of the HFR reactor (ELIMA 2).

In the experiment ELIMA 1 $Li_2SiO_3$ and $Li_4SiO_4$ pellets manufactured at KfK/IMF have been irradiated in the fast neutron flux of the KNK II reactor in Karlsruhe (Germany). The ultimate compressive strength and the Young's modulus of the irradiated pellets from all experiments have been measured in the Hot Cell Department of KfK.

## 2 Experimental

### 2.1 Materials Investigated

Tab. 1 gives an overview on the materials investigated, their manufacturers, and the test matrix in the irradiation experiment COMPLIMENT. The pellet dimensions were about 5 mm diameter x 5 mm length. The pellet columns were about 40 mm long and were sheathed in 1.4970 stainless steel tubes of 100 mm total length. All pellets were encapsulated under identical conditions at KfK/IMF. After being thoroughly dried they were filled into the tubes in a dry helium atmosphere at 300 °C and finally sealed by a welded end cap /1/. The $Li_2SiO_3$ and $Li_4SiO_4$ pellets irradiated in the ELIMA 1 experiment had the same dimensions and the same densities as in the COMPLIMENT irradiations.

In the following the mechanical properties of the materials before irradiation are given. The lithium silicate pellets manufactured at KfK are the only materials the mechanical properties of which, ultimate compressive strength and Young's modulus, have been measured under the same test conditions before and after irradiation. In all other cases the properties of the unirradiated materials have been taken from the literature or have been calculated considering their densities using correlations given in the literature.

Tab. 1: Test matrix of the irradiation experiment COMPLIMENT (taken from /1/)

| Manufacturer of the pellets | ELIMA 2/HFR-Petten | | DELICE 03/OSIRIS-Saclay | |
|---|---|---|---|---|
| | Matrix I 400 - 450 °C | Matrix II 650 - 700 °C | Matrix III 400 - 450 °C | Matrix IV 650 - 700 °C |
| CEA, Saclay | $LiAlO_2$ 78%[1], 139[2] | $LiAlO_2$ 78%, 143 | $LiAlO_2$ 78%, 147 | $LiAlO_2$ 78%, 151 |
| | $LiAlO_2$ 78%, 140 | $LiAlO_2$ 78%, 144 | $LiAlO_2$ 78%, 148 | $LiAlO_2$ 78%, 152 |
| | $LiAlO_2$ 62%, 141 | $LiAlO_2$ 62%, 145 | $LiAlO_2$ 62%, 149 | $LiAlO_2$ 62%, 153 |
| | $LiAlO_2$ 84%, 142 | $LiAlO_2$ 84%, 146 | $LiAlO_2$ 84%, 150 | $LiAlO_2$ 84%, 154 |
| ENEA, Cassacia | $LiAlO_2$ 80%, 117 | $LiAlO_2$ 80%, 120 | $LiAlO_2$ 80%, 155 | $LiAlO_2$ 80%, 158 |
| | $LiAlO_2$ 80%, 118 | $LiAlO_2$ 80%, 121 | $LiAlO_2$ 80%, 156 | $LiAlO_2$ 80%, 159 |
| | $LiAlO_2$ 80%, 119 | $LiAlO_2$ 80%, 122 | $LiAlO_2$ 80%, 157 | $LiAlO_2$ 80%, 160 |
| UKAEA Springfield | $Li_2O$ 83%, 131 | $Li_2O$ 80%, 133 | $Li_2O$ 79%, 135 | $Li_2O$ 82%, 137 |
| | $Li_2O$ 79%, 132 | $Li_2O$ 82%, 134 | $Li_2O$ 81%, 136 | $Li_2O$ 82%, 138 |
| | $Li_2ZrO_3$ 80%, 123 | $Li_2ZrO_3$ 80%, 125 | $Li_2ZrO_3$ 80%, 127 | $Li_2ZrO_3$ 80%, 129 |
| | $Li_2ZrO_3$ 80%, 124 | $Li_2ZrO_3$ 80%, 126 | $Li_2ZrO_3$ 80%, 128 | $Li_2ZrO_3$ 80%, 130 |
| CEN, Mol | $Li_2SiO_3$ 82%, 161 | $Li_2SiO_3$ 82%, 162 | $Li_2SiO_3$ 82%, 167 | $Li_2SiO_3$ 82%, 168 |
| | $Li_2SiO_3$ 82%, 163 | $Li_2SiO_3$ 75%, 166 | $Li_2SiO_3$ 82%, 169 | $Li_2SiO_3$ 75%, 172 |
| | $Li_2SiO_3$ 75%, 165 | $Li_2ZrO_3$ 80%, 164 | $Li_2SiO_3$ 75%, 171 | $Li_2ZrO_3$ 80%, 170 |
| KfK, Karlsruhe | $Li_4SiO_4$ 90%, 109 | $Li_4SiO_4$ 90%, 110 | $Li_4SiO_4$ 90%, 111 | $Li_4SiO_4$ 90%, 112 |
| | $Li_2SiO_3$ 90%, 101 | $Li_2SiO_3$ 90%, 102 | $Li_2SiO_3$ 90%, 103 | $Li_2SiO_3$ 90%, 104 |

[1] theoretical density
[2] KfK rod number

### 2.1.1 $Li_2SiO_3$

$Li_2SiO_3$ was supplied by two laboratories: KfK, Karlsruhe and CEN, Mol. The fabrication process of the KfK pellets is described in /1/. A detailed summary of the mechanical properties of $Li_2SiO_3$ manufactured at KfK, as ultimate compressive strength, Young's modulus, thermal shock behaviour, and creep rates under uniaxial compressive load in the temperature range between 800 and 900 °C, is given in /2/. No values of ultimate compressive strength and Young's modulus are available for the CEN material.

The following data and properties of the KfK pellets used in the irradiation experiments COMPLIMENT and ELIMA 1 have been measured:

Mean pellet diameter: 4.51 mm /3/
Mean grain diameter: 19 µm /3/
Density: 93.7% TD
Ultimate compressive strength: 288 ± 35 MPa
Young's modulus: 89 ± 2 GPa
Poisson's ratio: 0.22

Based on test results of several laboratory manufacturing series with different densities and grain sizes the following expression for the ultimate compressive strength has been derived

$$\sigma_c = 1600\,(1-P)^{3.5}\,d^{-0.45}\,. \tag{1}$$

$\sigma_c$ ultimate compressive strength in MPa
P relative porosity
d average grain size in μm

The best fit for the Young's modulus was found to be

$$E = 110\,(1-P)^3\,, \quad \text{GPa}\,. \tag{2}$$

These relations have been used to estimate the ultimate compressive strength and the Young's modulus of the CEN $Li_2SiO_3$ for porosities of 25% and 18%, respectively, and a mean grain size of 5 μm. For estimating the decrease in strength and Young's modulus the following data before irradiation have been calculated:

$Li_2SiO_3$ (CEN) 82% TD: $\sigma_c$ = 387 MPa, E = 61 GPa
$Li_2SiO_3$ (CEN) 75% TD: $\sigma_c$ = 283 MPa, E = 46 GPa

### 2.1.2 $Li_4SiO_4$

$Li_4SiO_4$ was supplied only by KfK. The fabrication process of the pellets is described in /1/. A detailed summary of the mechanical properties is given in /2/. The following data and properties of the pellets used in the irradiation experiments COMPLIMENT and ELIMA 1 have been measured:

Mean pellet diameter: 4.97 mm /3/
Mean grain diameter: 45 μm /3/
Density: 90.0% TD /3/
Ultimate compressive strength: 221 ± 39 MPa
Young's modulus: 79 ± 2 GPa
Poisson's ratio: 0.25

Based on test results of several laboratory manufacturing series with different densities and grain sizes the following expression for the ultimate compressive strength has been derived

$$\sigma_c = 975\,(1-P)^{1.5}\,d^{-0.44}\,. \tag{3}$$

The porosity dependence of the Young's modulus was found to be identical with that of the $Li_2SiO_3$ (Equ. 2).

### 2.1.3 $LiAlO_2$

$LiAlO_2$ pellets were supplied by two laboratories: CEA, Saclay and ENEA, Cassacia. The main characteristics and properties of the three different types of $\gamma$-$LiAlO_2$ pellets produced by ENEA are given in Table 2. All types were sintered to a density of 80%. The ultimate compressive strength of the CEA pellets has been estimated from CEA and KfK measurements to $\sigma_c$ = 290 MPa.

Tab. 2: Average grain size and mechanical properties of γ-$LiAlO_2$ (ENEA) /4/

| Type | Grain size µm | Bending strength MPa | Compressive strength MPa | Young's modulus GPa |
|---|---|---|---|---|
| P | 0.6 | 60 | 317 | 80.4 |
| A-1 | 0.4 and 10 (bimodal) | 48 | 222 | 46.2 |
| A-2 | 12 | - | 64 | 65.6 |

### 2.1.4 $Li_2ZrO_3$

$Li_2ZrO_3$ pellets were supplied by two laboratories: UKAEA, Springfield and CEN, Mol. The ultimate compressive strength of $Li_2ZrO_3$ pellets with a density of 80% TD and with a mean grain size of about 2 µm manufactured at UKAEA is given in /5,6/:

$$\sigma_c = 230 \pm 31 \text{ MPa}.$$

The following correlation for the Young's modulus is given in /7/:

$$E = 203.35\,(1-P)\,(1-1.286P)^2\,[1-2.40\cdot 10^{-4}\,(T-293)], \quad \text{GPa}. \tag{4}$$

E Young's modulus in GPa
P relative porosity
T temperature in K

No mechanical property data are available in the open literature for the CEN material.

## 2.2 Methods of Investigation

Usually, 4 or 5 pellets of each sample column were available for measuring the mechanical properties after irradiation. One of these pellets was used for the determination of the Young's modulus. In all those cases, where the number of available pellets was smaller, because pellets showed visible cracks or were used for other investigations, respectively, only the ultimate compressive strength was measured.

### 2.2.1 Compressive Strength

The ultimate compressive strength was measured in the Hot Cell Department of KfK using a Zwick universal testing machine type 1474. The pellets were loaded axially until failure occured. The load was applied at a rate of 100 N/s (~5 MPa/s). Each pellet was packed into two sealed plastic bags in order to prevent tritium release to the laboratory. Moreover, the two plastic foils between the pellets and the push rods compensated the relief and reduced the friction. The compressive strength of the unirradiated lithium silicate pellets was measured at KfK/IMF with the same load rate using a machine type INSTRON 8062.

### 2.2.2 Elastic Constants

The elastic constants have been determined by the ultrasonic pulse-echo method. A Krautkrämer instrument USIP 12 has been used. The longitudinal and share wave velocities were measured. Young's modulus and Poisson's ratio were evaluated from the measured sound velocities using the following relations

$$E = v_l^2 \rho \frac{(1+\mu)(1-2\mu)}{1-\mu}, \quad \text{GPa} \tag{5}$$

with the Poisson's ratio

$$\mu = \frac{0{,}5\, v_l^2 - v_t^2}{v_l^2 - v_t^2} \tag{6}$$

$v_l$ velocity of the longitudinal sound waves, km/s
$v_t$ velocity of the transverse sound waves, km/s
$\rho$ density, g/cm$^3$

The velocity of the longitudinal sound waves was measured using a 10 MHz ultrasonic probe. For measuring the velocity of the transverse sound waves a 4 MHz probe was used. The density has been evaluated by determination of the mass by weighing and of the volume by measuring the mean values of the diameter and of the height.

## 2.3 Irradiation Conditions

The irradiation experiment COMPLIMENT consists of test groups: DELICE 03 and ELIMA 2. DELICE 03 is the irradiation in the thermal neutron flux of the OSIRIS reactor in Saclay (France) and ELIMA 2 is the irradiation in the epithermal neutron flux of the HFR reactor in Petten (The Netherlands). The scheduled irradiation conditions are given in Tab. 3. The objectives of COMPLIMENT were (1) to study the irradiation behaviour of the different materials under the same test conditions, as neutron fluxes and temperatures, and (2) to compare the radiation damage in the materials caused by fast neutrons with the damage caused by the α- and tritium particles from the $^6$Li(n,α)$^3$H-reaction /1,8,9/. At nearly the same total damage doses in the two reactors the predominant damaging processes were different. The contribution of the n,α-reaction was high under the DELICE 03 thermal irradiation conducted in the OSIRIS reactor whereas it was relatively low in a epithermal flux of the HFR reactor.

The experiment ELIMA 1 is an irradiation of lithium silicates in the fast neutron flux of the Karlsruhe breeder reactor KNK II. The main objective of the KNK irradiation was to achieve higher damage rates due to fast neutrons. Again, temperature ranges of 400-450 °C and 650-700 °C were scheduled. However, in the high temperature capsules the 650-700 °C have been attained only for short periods. The mean temperature was about 620 °C. The irradiation capsules for the two temperature ranges are shown in /10/. The most important irradiation data of ELIMA 1 are also listet in Tab. 3.

Tab. 3: Scheduled irradiation data of the experiment COMPLIMENT /9/ and ELIMA 1 /11/

| | ELIMA 2 | DELICE 03 | ELIMA 1 |
|---|---|---|---|
| Test reactor<br>Neutron flux | HFR/Petten<br>epithermal<br>(Cd-screened) | OSIRIS/Saclay<br>thermal | KNK/Karlsruhe<br>fast |
| Beginning of irradiat. | April 1988 | October 1988 | January 1988 |
| End of irradiation | January 1989 | February 1989 | August 1991 |
| Full power days (FPD) | 178 | 77 | 144 |
| Lithium burnup, at.-% | ~0.25 | ~1.4 | ~1.2 |
| Radiation damage | | | |
| by fast neutrons | 1.6 dpa | 1.1 dpa | ~2 dpa |
| by ($\alpha$ + T) particles | 0.2 dpa | 0.7 dpa | ≤1 dpa |
| total | 1.8 dpa | 1.8 dpa | ≤3 dpa |

For the experiment ELIMA 2 the actual irradiation data of each sample are given in /12/. For this test group these Li-burnup values have been used for plotting strength vs. burnup. For the other experiments no reports on the data of the irradiations are available up to now. Therefore, the scheduled burnups and temperatures were used for the DELICE 03 and ELIMA 1 irradiations. The total heat production rate in ELIMA 2, e.g. the sum of the heat release rates by the $^6$Li(n,$\alpha$)$^3$H-reaction and by the absorption of $\gamma$-quanta, was in the range from 7 to 16 W/cm$^3$ depending on the position in the reactor and on the Li density of the material /12/. The temperature values have been estimated by interpolating measured temperatures in positions near the samples given in /13/. The values have been averaged over all irradiation cycles. The most important irradiation data of the ELIMA 2 experiment are summarized in Tab. 4. Only data of rods from which values of strength or of Young's modulus have been obtained are listed. The real data of Li-burnup and total damage dose are generally somewhat higher than the scheduled data.

In the DELICE 03 irradiation the heat production rate was much higher than in ELIMA 2. Based on the data of the Tritium generation and the relation for the power density by (n,$\alpha$)-reactions

$$q = 7.66 \cdot 10^{-13}\, p, \quad 1/\text{cm}^3\text{s} \tag{7}$$

p Tritium production rate

given in /14/ the total heat production rate, including a gamma heating of ≤5 W/cm$^3$, was estimated to be in the range from 40 W/cm$^3$ for $Li_2SiO_3$ (sample P 117) to 140 W/cm$^3$ for $Li_2O$ (P133).

Tab. 4: Irradiation data of the experiment ELIMA 2 (temperatures evaluated from /13/, damage, burnup, and heat generation rate Q taken from /12/)

| Material, Manufacturer | Matrix I | | | | | Matrix II | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Rod | Temp. °C | dpa total | Bu % Li | Q W/cm³ | Rod | Temp. °C | dpa total | Bu % Li | Q W/cm³ |
| $LiAlO_2$, CEA | 139 | 485 | 2.86 | 0.45 | 9.8 | 144 | 690 | 2.95 | 0.46 | 7.5 |
| $LiAlO_2$, ENEA | 118 | 470 | 2.31 | 0.36 | 8.0 | 120 | 690 | 3.02 | 0.47 | 10.5 |
| | 119 | 475 | 2.52 | 0.39 | 8.8 | 121 | 695 | 3.02 | 0.47 | 10.5 |
| | | | | | | 122 | 640 | 2.34 | 0.37 | 8.2 |
| $Li_2ZrO_3$, UKAEA | 123 | 450 | 1.61 | 0.31 | 10.3 | 125 | 640 | 2.58 | 0.49 | 16.7 |
| | 124 | 490 | 2.38 | 0.45 | 15.4 | 126 | 685 | 1.94 | 0.37 | 12.6 |
| $Li_2ZrO_3$, CEN | | | | | | 164 | 685 | 2.12 | 0.40 | 13.7 |
| $Li_2SiO_3$, CEN | 161 | 440 | 1.88 | 0.35 | 9.3 | 163 | 640 | 2.72 | 0.50 | 13.5 |
| | 162 | 485 | 2.44 | 0.45 | 12.0 | 166 | 640 | 2.58 | 0.48 | 11.7 |
| | 165 | 440 | 1.97 | 0.35 | 8.5 | | | | | |
| $Li_2SiO_3$, KfK | 101 | 455 | 1.98 | 0.36 | 10.6 | 102 | 690 | 2.82 | 0.37 | 12.2 |
| $Li_4SiO_4$, KfK | 109 | 455 | 1.37 | 0.28 | 9.1 | 110 | 635 | 1.81 | 0.38 | 12.2 |

## 2.4 Test Results

### 2.4.1 Compressive Strength

The irradiation data and the compressive strengths of the materials irradiated in the COMPLIMENT and ELIMA 1 experiments are listed in Tab. 5. The mean values with standard deviation und the maximum values are given. The number in paranthesis is the number of the pellets tested. The mean values possibly are lower than the 'true' strength values, because all uncertainties, e.g. not plane-parallel faces or cracks not detected, reduce the measured strength. In Tab. 5 also the mean densities of the pellets investigated are presented. In the Fig. 1 to 4 the compressive strengths of $LiAlO_2$, $Li_2ZrO_3$, $Li_2SiO_3$, and $Li_4$SiO4 are plotted versus Li-burnup. For $Li_2O$ only values after irradiation to about 0.37% Li-burnup at 685 °C have been measured. Some of the results of the COMPLIMENT experiment have been published earlier /15,16/.

Tab. 5: Compressive strengths of the materials irradiated in the COMPLIMENT and ELIMA 1 experiments

| Material, Manufacturer, Theor. density | Rod No. | Mean temp. °C | Damage dose dpa | | Li-burnup % | Mean density g/cm³ | Compressive strength, MPa | |
|---|---|---|---|---|---|---|---|---|
| | | | $n_{fast}$ | total | | | mean | max. |
| $LiAlO_2$, CEA, 78% | P 139 | 485 | 2.77 | 2.86 | 0.45 | 1.79 | 83 ± 10 (3) | 91 |
| | P 144 | 690 | 2.86 | 2.95 | 0.46 | 2.18 | 245 ± 22 (4) | 264 |
| | P 151 | 650-700 | ~1.1 | ~1.8 | ~1.4 | 1.98 | 193 (1) | 193 |
| | P 152 | 650-700 | ~1.1 | ~1.8 | ~1.4 | 2.12 | 171 (1) | 171 |
| $LiAlO_2$, ENEA, 80% P | P 118 | 470 | 2.24 | 2.31 | 0.36 | 2.09 | 174 ± 9 (4) | 185 |
| A1 | P 121 | 695 | 2.93 | 3.02 | 0.47 | 2.15 | 142 ± 10 (5) | 154 |
| $Li_2O$, UKAEA, 80% | P 133 | 685 | 1.21 | 1.35 | 0.38 | 1.63 | 78 ± 12 (4) | 93 |
| 82% | P 134 | 685 | 1.15 | 1.30 | 0.36 | 1.57 | 91 ± 8 (3) | 100 |
| $Li_2ZrO_3$, UKAEA, 80% | P 123 | 450 | 1.54 | 1.61 | 0.31 | 3.34 | 204 ± 30 (6) | 252 |
| | P 124 | 490 | 2.27 | 2.38 | 0.45 | 3.30 | 167 ± 37 (4) | 212 |
| | P 127 | 400-450 | ~1.1 | ~1.8 | ~1.4 | 3.19 | 97 ± 37 (3) | 139 |
| | P 128 | 400-450 | ~1.1 | ~1.8 | ~1.4 | 3.21 | 135 ± 48 (3) | 164 |
| | P 125 | 640 | 2.46 | 2.58 | 0.49 | 3.24 | 124 ± 14 (7) | 138 |
| | P 126 | 685 | 1.85 | 1.94 | 0.37 | 3.22 | 111 ± 42 (3) | 160 |
| | P 129 | 650-700 | ~1.1 | ~1.8 | ~1.4 | 3.24 | 161 ± 23 (2) | 177 |
| | P 130 | 650-700 | ~1.1 | ~1.8 | ~1.4 | 3.12 | 74 ± 20 (4) | 101 |
| $Li_2ZrO_3$, CEN, 80% | P 164 | 685 | 2.02 | 2.12 | 0.40 | 3.23 | 83 ± 3 (5) | 88 |
| | P 170 | 650-700 | ~1.1 | ~1.8 | ~1.4 | 3.25 | 116 ± 11 (5) | 133 |
| $Li_2SiO_3$, CEN, 82% | P 162 | 485 | 2.34 | 2.44 | 0.45 | 1.98 | 270 ± 5 (3) | 275 |
| 75% | P 165 | 440 | 1.89 | 1.97 | 0.35 | 1.82 | 168 ± 27 (8) | 200 |
| 82% | P 169 | 400-450 | ~1.1 | ~1.8 | ~1.4 | 1.89 | 162 ± 6 (3) | 169 |
| 82% | P 163 | 640 | 2.61 | 2.72 | 0.50 | 1.98 | 194 ± 31 (5) | 234 |
| 75% | P 166 | 640 | 2.47 | 2.58 | 0.48 | 1.87 | 166 ± 12 (5) | 183 |
| 75% | P 172 | 650-700 | ~1.1 | ~1.8 | ~1.4 | 1.85 | 127 ± 42 (6) | 161 |
| $Li_2SiO_3$, KfK, 90% | P 101 | 455 | 1.90 | 1.98 | 0.36 | 2.26 | 86 ± 8 (3) | 94 |
| | P 103 | 400-450 | ~1.1 | ~1.8 | ~1.4 | 2.17 | 64 ± 2 (3) | 66 |
| | P 102 | 690 | 2.73 | 2.82 | 0.37 | 2.14 | 99 ± 40 (3) | 145 |
| | P 104 | 650-700 | ~1.1 | ~1.8 | ~1.4 | 2.18 | 82 ± 8 (4) | 89 |
| | MHT 40 | ~620 | ~2 | ≤3 | <1 | 2.14 | 71 ± 14 (4) | 91 |
| | MHT 24 | ~620 | ~2 | ≤3 | <1 | 2.17 | 89 ± 14 (5) | 111 |
| $Li_4SiO_4$, KfK, 90% | P 109 | 455 | 1.29 | 1.37 | 0.28 | 2.00 | 50 (1) | 50 |
| | P 110 | 635 | 1.70 | 1.81 | 0.38 | 1.84 | 63 ± 10 (2) | 69 |
| | OHT 6 | ~620 | ~2 | ≤3 | <1 | 2.01 | 67 ± 10 (3) | 73 |
| | OHT 8 | ~620 | ~2 | ≤3 | <1 | 2.03 | 86 ± 20 (3) | 109 |

At irradiation temperatures below 490 °C the compressive strength of the $LiAlO_2$ shows a very strong dependence on the Li-burnup at low burnup levels. This is true both for the ENEA P material (80% TD) and for the CEA material (78% TD). Though pellet integrity was good after decladding some microcracks have been found in both materials after irradiation in the temperature range from 400 to 450 °C (Fig. 5). The extremely low strength of $LiAlO_2$ (CEA) in rod 139 is mainly caused by the very low density after irradiation. Unfortunately, no ceramographic examination on pellets from this rod has been performed which could give more detailed information on porosity and crack structure of this material. At irradiation temperatures in the range from 650 to 700 °C the decrease rate in strength is much smaller. Independent of the Li-burnup the compressive strength is reduced to 59-67% of its initial value.

The silicate pellets, $Li_4SiO_4$ and $Li_2SiO_3$ (KFK), exhibit the largest decrease in strength of all materials investigated. At all irradiation conditions the residual strength is reduced to <35% of its initial value. This seems to be primarily caused by the formation of cracks and microcracks, especially in $Li_4SiO_4$. Fig. 6 shows micrographs of a $Li_4SiO_4$ pellet irradiated in the HFR reactor at 455 °C to 0.28% Li-burnup. The $Li_2SiO_3$ pellets supplied by CEN exhibit a much finer grain structure and a less extensive microcracking than the KfK material. The relative strength reduction of the CEN material is smaller than that of the KfK material. The residual strength after irradiation always is >40% of its initial value. The temperature dependence of the strength reduction is not uniform for the various silicates. All KfK materials, both $Li_4SiO_4$ and $Li_2SiO_3$, and the 75% dense CEN $Li_2SiO_3$ show the larger reduction in the 440-455 °C range. Whereas the 82% dense CEN $Li_2SiO_3$ exhibits the larger reduction at 640 °C.

$Li_2ZrO_3$ seems to be the material the strength of which decreases more slightly with the Li-burnup than that of other materials. There is a remarkable difference between the strengths of the pellets in the capsules P 129 and P 130 though the scheduled irradiation data of the two capsules are the same. However, the as-irradiated densities of the pellets are somewhat different. Possibly, the difference is attributed to different irradiation temperatures. Comparing the irradiation data and the values of strength and density of the ELIMA 2 capsules P 123/P 124 and P 125/P 126, respectively, it is evident that a higher irradiation temperature contributes significantly to a reduction in strength and density. The compressive strength of $Li_2ZrO_3$ pellets from various capsules is plotted versus their density in Fig. 7. The results indicate that there must be a difference in the irradiation temperatures between the capsules P 129 and P 130. The materials provided by UKAEA and CEN have the same (nominal) initial density and are irradiated under the same conditions. However, the strength of the CEN $Li_2ZrO_3$ after irradiation is somewhat lower than that of the UKAEA $Li_2ZrO_3$. The grain size of the CEN material is not known, so that the differences cannot be discussed.

The compressive strength of $Li_2O$ after irradiation is one of the lowest. However, the strength in the as-fabricated state is also low. If we assume a value of 132 MPa given in /5/ for a material with 80% density used in other irradiation experiments, the relative strength reduction to 59% after irradiation at 685 °C to about 0.4% Li-burnup is the same as measured for $Li_2ZrO_3$ (UKAEA) and $Li_2SiO_3$ (CEN).

## 2.4.2 Young's Modulus

The results of the Young's modulus determinations are listed in Tab. 6. Values of the Poisson's ratio are given only, if the velocity of the transverse sound waves could be measured. Sometimes these measurements were impossible due to high damping. In these cases the Poisson's ratios given in Tab. 7 (Chapter 3) have been used to calculate the Young's moduli.

A very low Young's modulus of 15 GPa has been found for the 83% dense $Li_2O$ irradiated at 450 °C to 0.27% Li-burnup. The density of this sample, which had a nominal initial density of 83%, was extremly low (1.36 g/cm$^3$ or 68% TD). The micrograph shown in Fig. 8 confirms this low density. Generally, the decrease of the Young's modulus under irradiation is small. Even a slight increase has been found for the $LiAlO_2$ (ENEA A1) which is obvious due to a slight increase in density. The other two types of $LiAlO_2$ (ENEA) exhibit a decrease with the Li-burnup (Fig. 9) at nearly constant density. No decrease of the Young's moduli has been observed for $Li_2ZrO_3$ (UKAEA) and $Li_2SiO_3$ (CEN) if there was no decrease in density. However, there is a marked reduction of the Young's modulus of $Li_2ZrO_3$ with decreasing density. In Fig. 10 the Young's moduli of various materials are plotted versus the density. As indicated by this Fig. the Young's modulus in the as-irradiated state seems to be a strong function of the density.

Tab. 6: Young's moduli of the materials irradiated in the COMPLIMENT and ELIMA 1 experiments

| Material, Manufacturer, Theor. density | Rod No. | Temp. °C | Total damage dose dpa | Li-burnup % | Density | | Young's modulus GPa | Poisson's ratio |
|---|---|---|---|---|---|---|---|---|
| | | | | | g/cm$^3$ | % TD | | |
| $LiAlO_2$, ENEA, 80% P | P 118 | 470 | 2.31 | 0.36 | 2.10 | 82 | 60 | 0.17 |
| A1 | P 157 | 400-450 | ~1.8 | ~1.4 | 2.08 | 82 | 52 | 0.14 |
| A2 | P 120 | 690 | 3.02 | 0.47 | 2.09 | 82 | 59 | - |
| A1 | P 121 | 695 | 3.02 | 0.47 | 2.13 | 84 | 51 | 0.17 |
| A1 | P 122 | 640 | 2.34 | 0.37 | 2.11 | 83 | 53 | - |
| P | P 158 | 650-700 | ~1.8 | ~1.4 | 2.15 | 84 | 67 | - |
| A2 | P 159 | 650-700 | ~1.8 | ~1.4 | 2.07 | 81 | 53 | - |
| A1 | P 160 | 650-700 | ~1.8 | ~1.4 | 2.13 | 83 | 49 | 0.17 |
| $Li_2O$, UKAEA, 83% | P 131 | 450 | 0.99 | 0.27 | 1.36 | 65 | 15 | - |
| 80% | P 133 | 685 | 1.35 | 0.38 | 1.63 | 77 | 79 | - |
| $Li_2ZrO_3$, UKAEA, 80% | P 123 | 450 | 1.61 | 0.31 | 3.40 | 82 | 89 | 0.21 |
| | P 126 | 685 | 1.94 | 0.37 | 3.22 | 78 | 59 | 0.19 |
| | P 127 | 400-450 | ~1.8 | ~1.4 | 3.16 | 76 | 58 | 0.21 |
| | P 129 | 650-700 | ~1.8 | ~1.4 | 3.34 | 80 | 93 | - |
| $Li_2SiO_3$, CEN, 82% | P 161 | 440 | 1.88 | 0.35 | 2.02 | 80 | 67 | 0.18 |
| | P 162 | 485 | 2.44 | 0.45 | 1.98 | 78 | 65 | 0.23 |
| $Li_4SiO_4$, KfK, 90% | OHT 6 | ~620 | ≤3 | <1 | 2.03 | 85 | 62 | - |
| | OHT 8 | ~620 | ≤3 | <1 | 2.05 | 86 | 64 | - |

## 3 Discussion

There is a number of possible mechanisms which can change the strength of ceramics under neutron irradiation: formation of lattice defects due to particle collisions, formation of gas bubbles and changes in composition as a result of nuclear transmutations, and crack formation caused by thermal stresses. Generally, the reduction of the strength observed after irradiation is the result of a more or less complex interaction of all these processes. The dominant mechanism depends on the irradiation conditions and may change from material to material.

Considering the dependence of the strength reduction of all materials investigated on damage doses due to fast neutrons and $\alpha$- and tritium particles from the $^6Li(n,\alpha)^3H$-reaction, respectively, it is evident that the Li-burnup is the deciding parameter. Apparently, gas formation (He and Tritium) and resulting phenomena from this, especially the formation of gas bubbles at grain boundaries which can result in the formation of cracklike intergranular separations, are more effective in strength reduction than radiation damages caused by fast neutrons. The fracture mode is intergranular as scanning electron microprobe analysis has revealed, only $Li_2SiO_3$ (KfK) exhibits intergranular and intragranular cracks /12/.

Crack formation due to thermal stresses during irradiation seems to be the most effective mechanism in strength reduction of the pellets. The resistance of the materials to crack formation under thermal loading expressed by the thermal shock parameter

$$R' = \frac{\sigma(1-\mu)\lambda}{E\alpha} \tag{8}$$

$\sigma$ ultimate tensile strength
$\mu$ Poisson's ratio
E Young's modulus
$\alpha$ thermal expansion coefficient
$\lambda$ thermal conductivity

is quite different. Values of R' for materials with 80% TD are given in Table 7. Concerning R' increasing resistance to thermal shock is indicated in the order: $Li_4SiO_4$, $Li_2SiO_3$, $Li_2O$, $Li_2ZrO_3$, $LiAlO_2$. In agreement with the ranking given by the thermal shock parameters the integrity of the pellets after decladding was best in $Li_2ZrO_3$ and $LiAlO_2$ (≥78% TD).

The silicates (KfK), especially $Li_4SiO_4$, show the most extensive crack structure and the largest reduction in strength. However, microcracks have been found also in $LiAlO_2$ (Fig. 5) irradiated in the temperature range from 400 to 450 °C. Possibly, these microcracks are the result of thermal shocks due to severe temperature drops by reactor shutdowns. As far as investigated, no microcracks were detected in $Li_2ZrO_3$, $Li_2SiO_3$ (CEN) and $Li_2O$ after irradiation in the HFR reactor (ELIMA 2). May be, the tendency of the $LiAlO_2$ to form microcracks is more marked at low irradiation temperatures. This could explain the larger decrease in strength at 400 to 450 °C than at 650 to 700 °C.

The influence of the irradiation temperature on the strength reduction seems to be different from material to material. $LiAlO_2$, the KfK silicates, and the 75% dense CEN $Li_2SiO_3$ exhibit the larger reduction in the 440-455 °C range. Whereas $Li_2ZrO_3$ and the 82% dense CEN $Li_2SiO_3$ show a slightly larger reduction at temperatures ≥640 °C. Possibly, the different behaviour is caused by

Tab. 7: Thermal shock parameters R' of the different materials irradiated in the COMPLIMENT experiment

| | $Li_4SiO_4$ | $Li_2SiO_3$ | $Li_2O$ | $Li_2ZrO_3$ | $LiAlO_2$ |
|---|---|---|---|---|---|
| Bending strength at RT, MPa | 38.8 /17/ | 40 [1] | 50.1 /17/ | 65 /17/ | 74.8 /17/ |
| Young's modulus at RT, GPa | 56.3 /17/ | 56 [2] | 70 /17/ | 89.8 /17/ | 75 /17/ |
| Poisson's ratio | 0.24 /17/ | 0.22 [2] | 0.19 /17/ | 0.2 /17/ | 0.22 /17/ |
| Thermal exp. coeff. (25-600 °C), $10^{-5}$/K | 2.45 /17/ | 2.1 /18/ | 2.61 /17/ | 0.99 /17/ | 1.08 /17/ |
| Thermal conductivity at 600 °C, W/mK | 0.82 /17/ | 2.00 /18/ | 3.54 /17/ | 1.42 /17/ | 2.83 /17/ |
| R', W/cm | 0.18 | 0.53 | 0.79 | 0.83 | 2.04 |

[1] estimated from KfK measurements of compressive strength using a value of 6 for the ratio of compressive strength to bending strength

[2] KfK measurement

different dependencies of the brittleness on temperature. It has been found, that the plasticity of $Li_2O$ single crystals increases remarkably above 330 °C /19/. Accordingly no cracks or microcracks have been found in this material. In nearly all cases the steepest decrease in strength occurs at Li-burnups ≤0,4 at-% indicating that crack formation contributes significantly to strength reduction.

The relative decrease of the Young's modulus under irradiation is always smaller than that of the compressive strength. Only for $LiAlO_2$ (ENEA type A1 and A2) a systematic dependence of the Young's modulus on the Li-burnup has been found. In all other cases the Young's moduli depend only on the actual values of the density as shown in Fig. 10. Of course, the density is a function of the irradiation conditions and of the initial pellet density, but the densities measured sometimes do not agree with the values expected based on the scheduled data. A densification during irradiation cannot be excluded for $LiAlO_2$ (ENEA) type A1 and P. For both materials the densities are higher after irradiation at 650-700 °C than after 400-450 °C.

Decreases in density and Young's modulus under irradiation are induced by the formation of gas bubbles, decohesions of grains, and microcracks. The time an ultrasonic impuls needs to pass through the sample is sensitive to details of the microstructure. Especially grain boundary separations increase the transit time much more than spherical bubbles, e.g. they are more effective in reducing ultrasonic velocity than density. Therefore, the dependence of the Young's modulus on the density shown in Fig. 10 is much stronger than given by any formula describing the dependence on porosity induced by fabrication processes.

## 4 Summary

The most important observations from the COMPLIMENT and ELIMA 1 experiments with respect to changes in mechanical properties of breeder ceramics during irradiation can be summarized as follows:

- A considerable reduction of the compressive strength has been found for all pellet materials. $Li_4SiO_4$ exhibits the largest decrease, the lowest one has been observed in $Li_2ZrO_3$ at all irradiation temperatures and in $LiAlO_2$ at 650-700 °C.
- The steepest decrease in strength occurs at Li-burnups $\leq$0,4 at-% indicating that crack formation is one of the most effective mechanism in strength reduction.
- Considering the dependence of the strength reduction on damage doses due to fast neutrons and $\alpha$- and tritium particles from the $^6Li(n,\alpha)^3H$-reaction, respectively, it is evident that the Li-burnup is the deciding parameter. Obviously gas formation and resulting phenomena from this are more effective in strength reduction than radiation damages caused by fast neutrons.
- The influence of the irradiation temperature on the strength decrease seems to be different from material to material caused by different dependencies of the brittleness on temperature.
- The relative reduction of the Young's modulus under irradiation is smaller than that of the compressive strength. It depends primarily on the actual values of the density after irradiation.

## Acknowledgment

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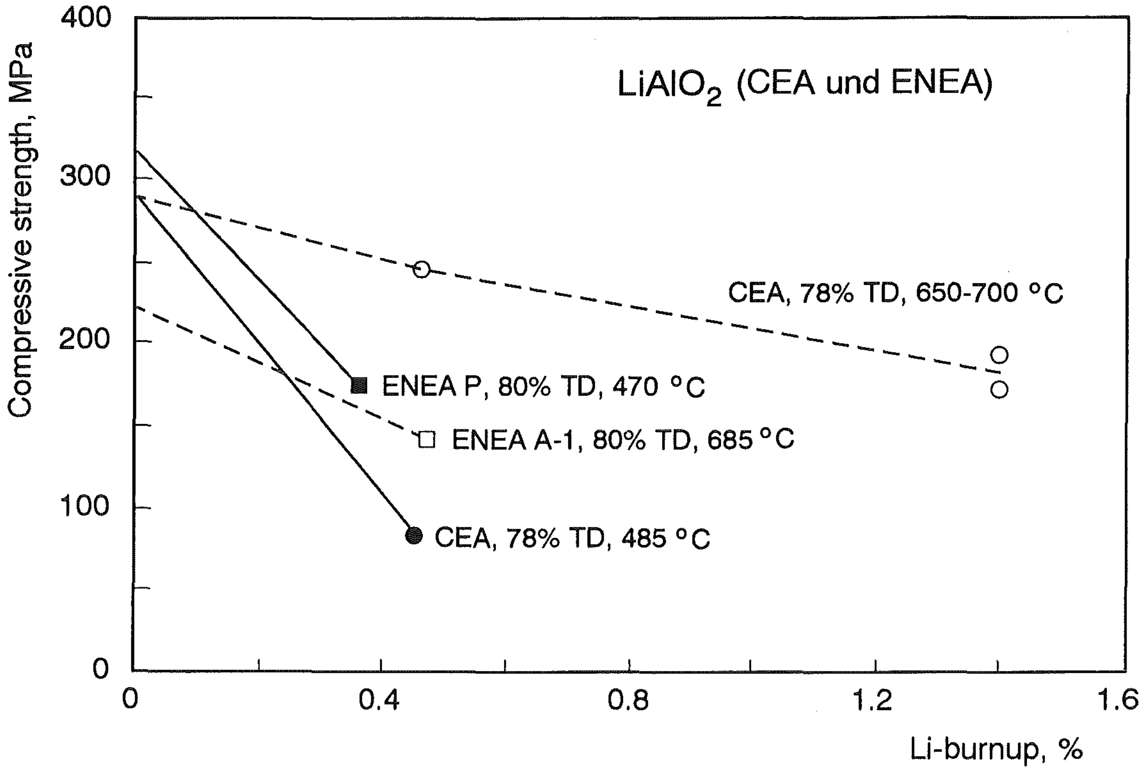

Fig. 1: Ultimate compressive strength of $LiAlO_2$, CEA and ENEA as a function of Li-burnup

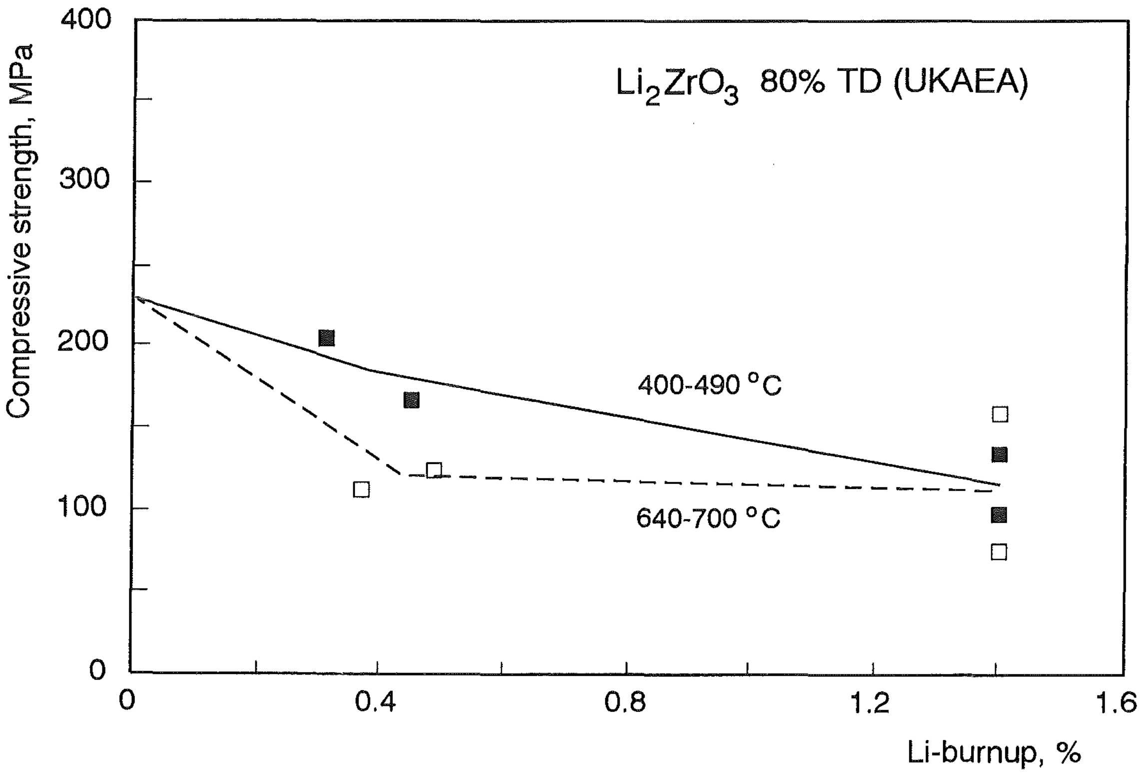

Fig. 2: Ultimate compressive strength of $Li_2ZrO_3$, UKAEA as a function of Li-burnup

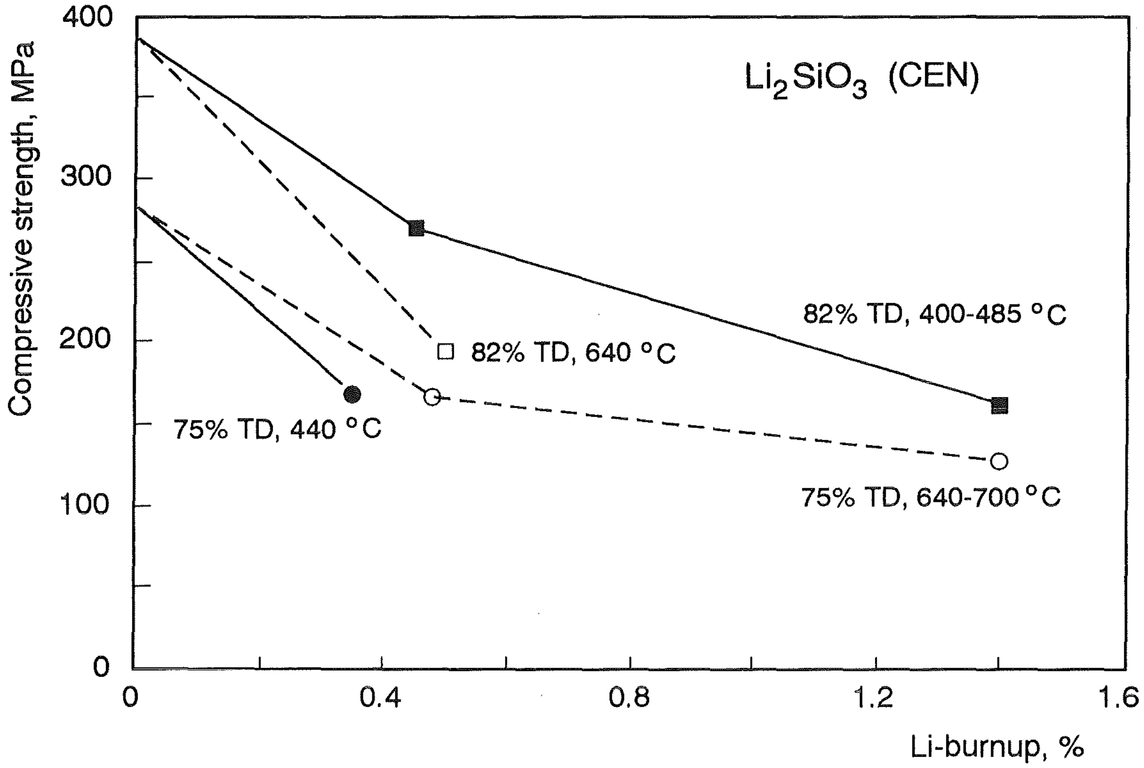

Fig. 3: Ultimate compressive strength of $Li_2SiO_3$, CEN as a function of Li-burnup

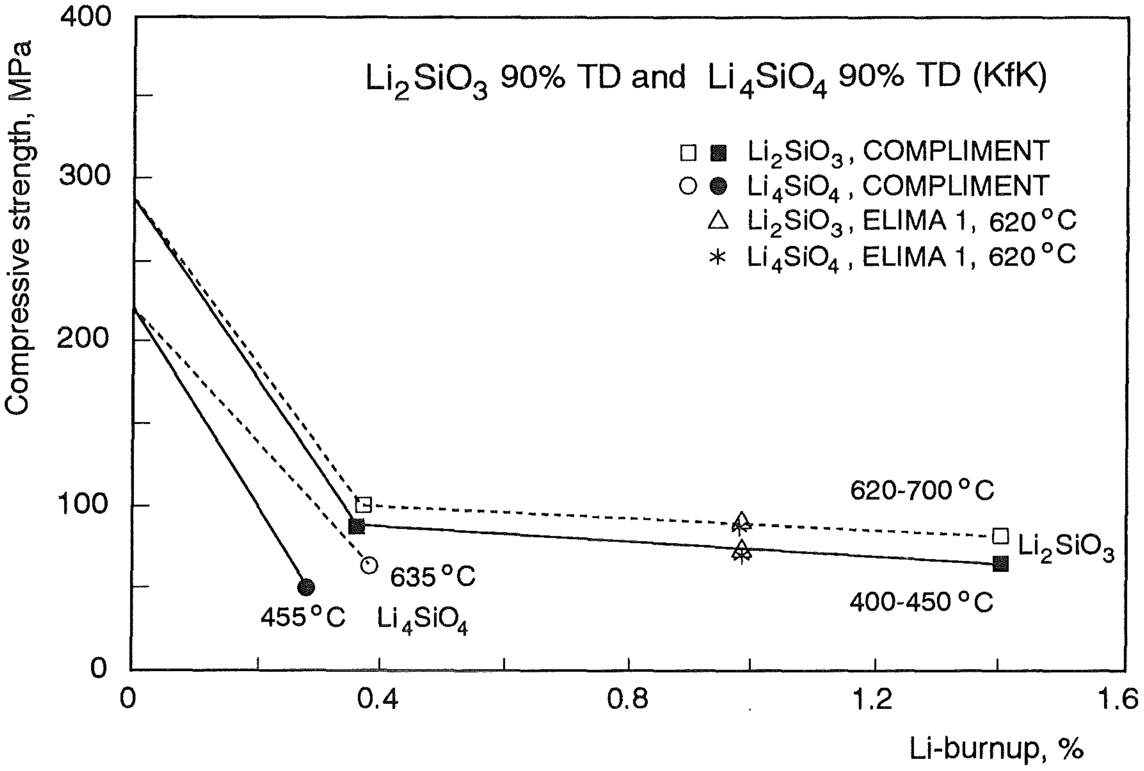

Fig. 4: Ultimate compressive strength of $Li_2SiO_3$, KfK and $Li_4SiO_4$, KfK as a function of Li-burnup

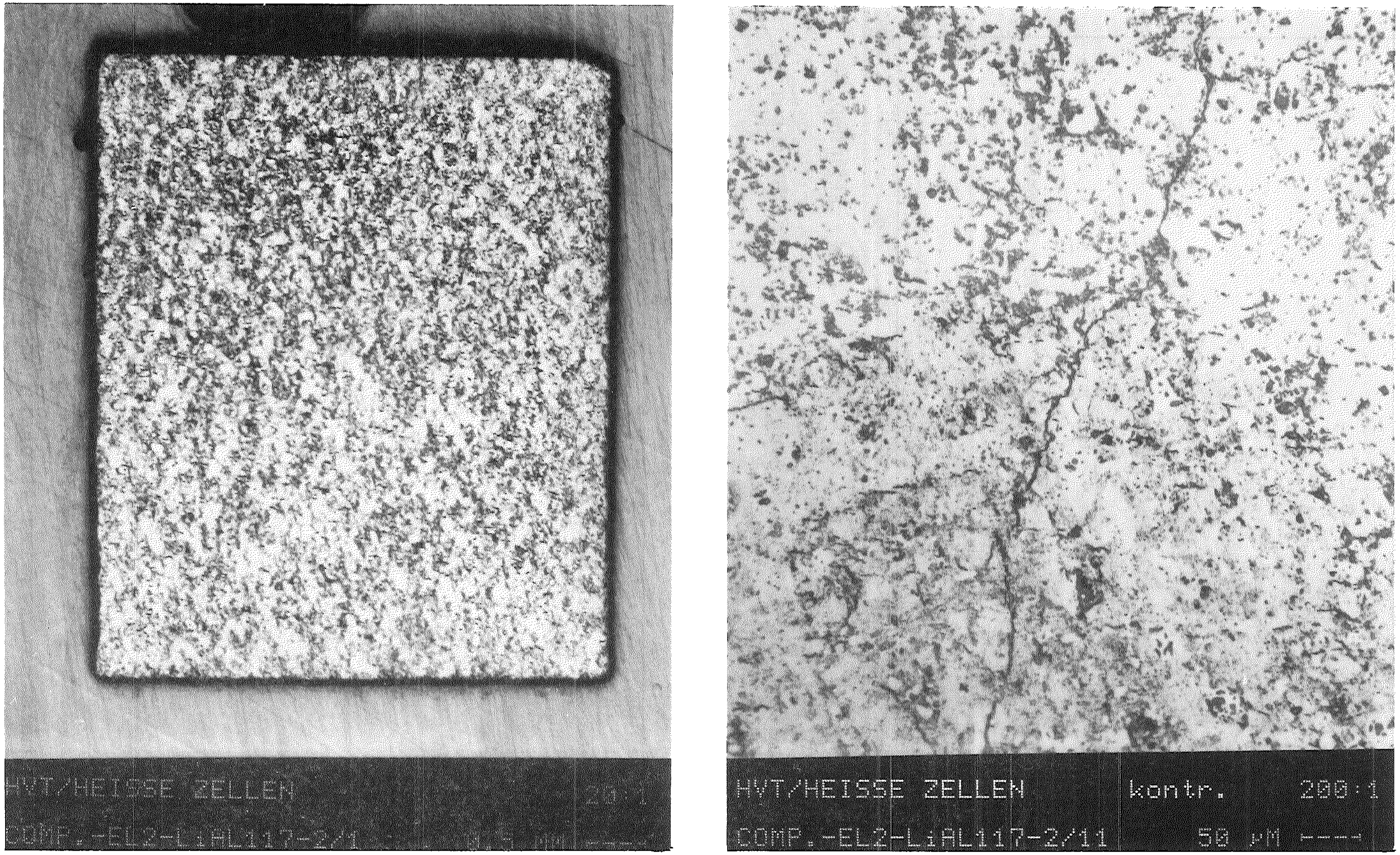

Fig. 5: Microstructure of $LiAlO_2$ (ENEA) irradiated in the HFR reactor at 440 °C to 0.28% Li-burnup

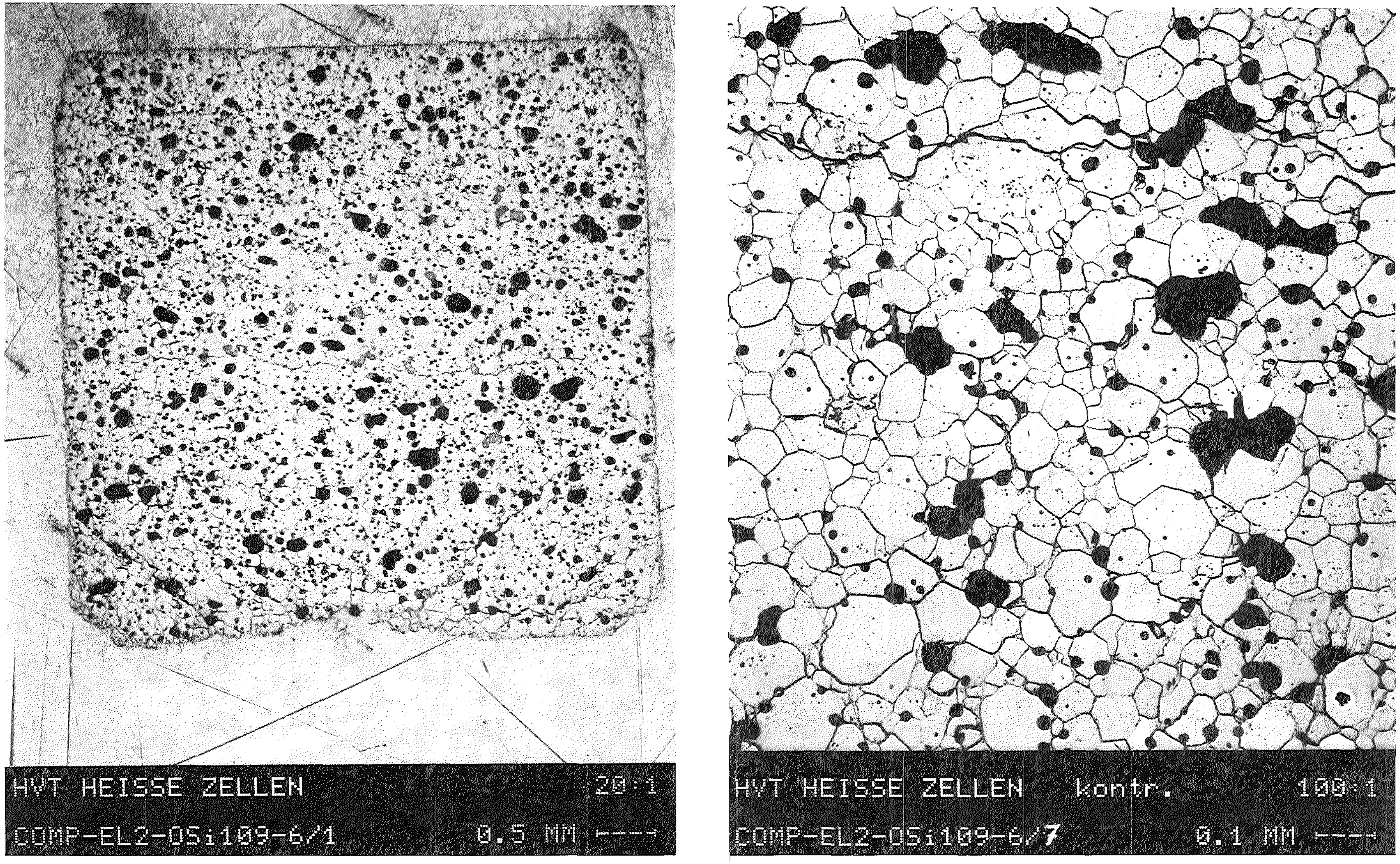

Fig. 6: Microstructure of $Li_4SiO_4$ irradiated in the HFR reactor at 474 °C to 0.36% Li-burnup

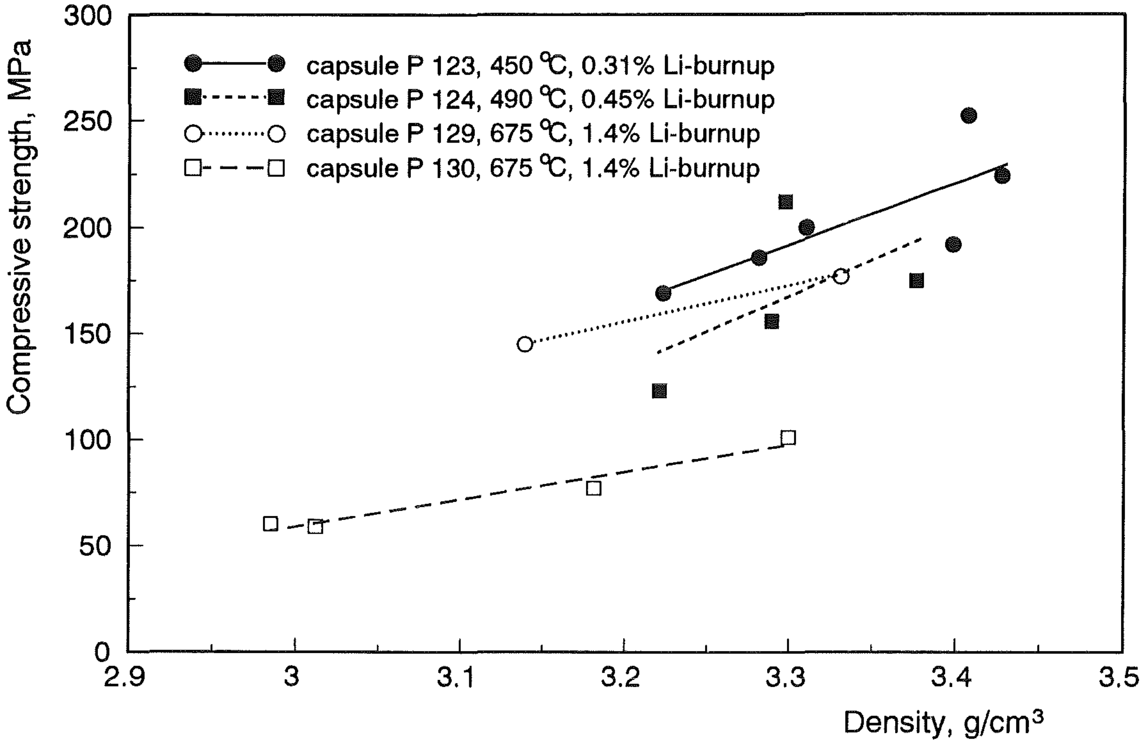

Fig. 7: Compressive strength of $Li_2ZrO_3$ (UKAEA) as a function of density

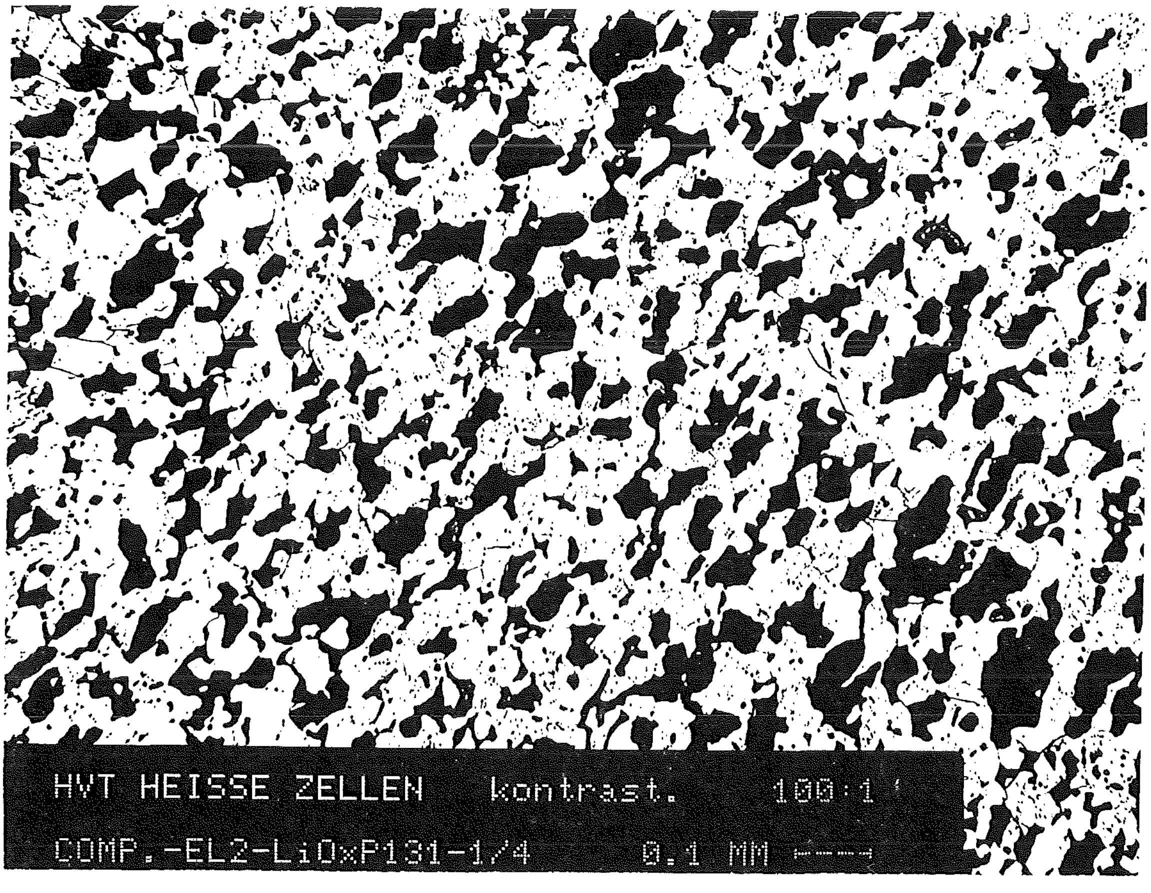

Fig. 8: Microstructure of $Li_2O$ irradiated in the HFR reactor at 458 °C to 0.27% Li-burnup

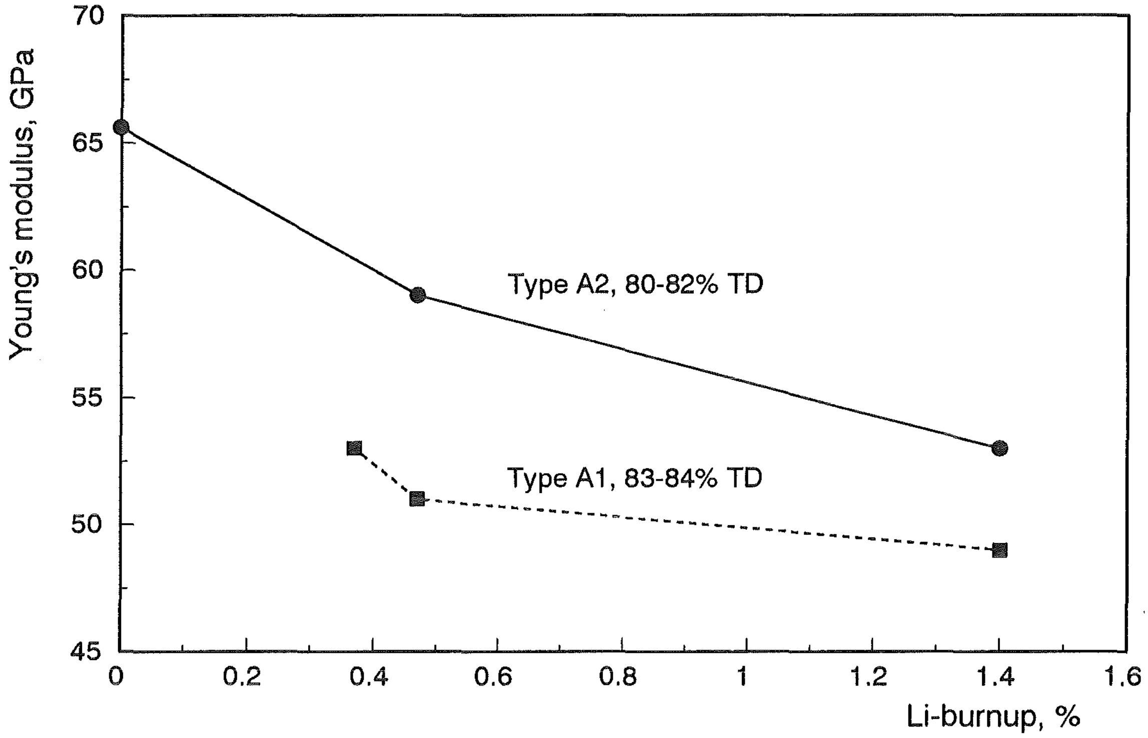

Fig. 9: Young's modulus of $LiAlO_2$ (ENEA) after irradiation at temperatures ≥640 °C as a function of Li-burnup

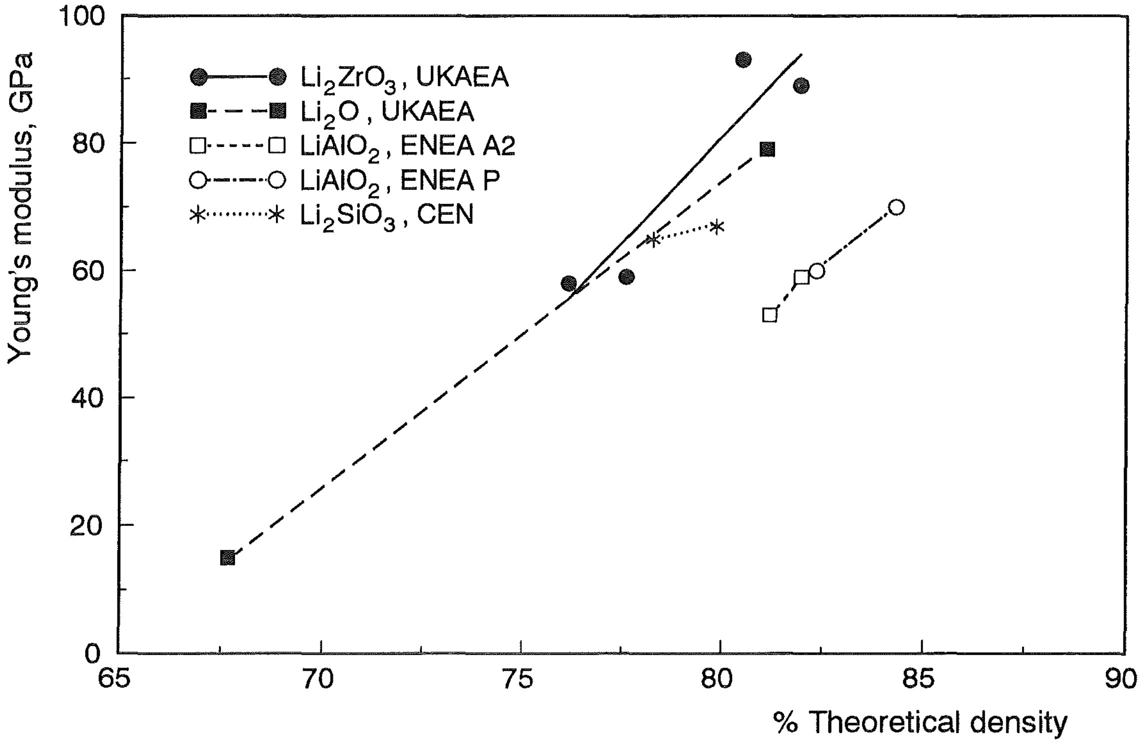

Fig. 10: Young's modulus of irradiated Li ceramics as a function of density